SYNTHESIS AND CHARACTERIZATION OF TRIDECAMERIC GROUP 13 HYDROXIDE CLUSTERS

by

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Title: SYNTHESIS AND CHARACTERIZATION OF TRIDECAMERIC GROUP 13 HYDROXIDE CLUSTERS

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In the research area of Group 13 hydroxide clusters, progress is often hampered by difficult and inefficient synthetic procedures. This has greatly limited the numerous potential applications of Group 13 hydroxide compounds, many of which require large amounts of material. Most relevant to this dissertation is their application as precursors for high quality amorphous metal oxide thin films. Addressing this issue, this dissertation presents a series of Group 13 containing hydroxide compounds of general formula $[M_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ which are generated through an efficient, scalable synthetic procedure. Throughout this dissertation, the compounds are generally referred to by their metal content, i.e. $[Ga_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ is designated as Ga_{13}. Chapter I reviews the literature of inorganic and ligand-supported

Group 13 hydroxide compounds with the aim of identifying common structural trends in metal composition and coordinating ligands. This summary is limited to clusters of aluminum, gallium, and indium. Chapter II describes in detail the synthesis and characterization of one such cluster, Al_{13}. Following this in Chapter III is the description of the first heterometallic Group 13 hydroxide compound, Ga_7In_6, which along with Ga_{13} was used as a precursor material for metal oxide thin films in collaboration with Professor Doug Keszler at Oregon State University. Chapter IV describes a series of six Ga/In compounds, as well as two Al/In compounds. Included in this chapter is an analysis of the heat-induced decomposition properties of the Ga/In clusters. Understanding such thermal decomposition is particularly relevant for the use of these compounds as precursor materials, as an annealing step is used to condense the films. Chapter V addresses the potential for post-synthetic modification of the compounds through metal and ligand exchange reactions, an area that also addresses the issue of solution stability of the structures. Chapter VI describes the synthesis and characterization of related Group 13 compounds, including two infinite chain structures and additional heterometallic compounds. Lastly, Chapter VII concludes this dissertation and discusses potential areas of future research.

This dissertation includes co-authored material and previously published results.

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CHAPTER I

OLIGOMERIC GROUP 13 HYDROXIDE COMPOUNDS – A RARE BUT VARIED CLASS OF MOLECULES

Introduction

Trivalent Group 13 metal ions such as aluminum, gallium, and indium exist as a wide and dynamic range of species in solution where they have been said to possess a "bewildering variety of behavior".[1] Aluminum has been by far the most widely studied of the group, with gallium and indium receiving less scrutiny. Much of the work in this area has focused on solution studies, with several recent reviews on this subject.[2-5] In contrast to the large body of work aimed at studying the complex solution speciation, the number of solid state examples of Group 13 hydroxides is relatively limited. This chapter seeks to provide a thorough summary of solid state Group 13 (aluminum, gallium, and indium) structures containing only octahedral metal ions bridged by hydroxide ligands. Both ligand-supported and fully inorganic clusters will be discussed. Ligand-supported compounds are those comprised of an inorganic metal hydroxide core with organic ligands (often aminocarboxylates) filling the peripheral coordination sites of the cluster ions.[6-8] The fully inorganic clusters are exactly that: metal hydroxide clusters with water most commonly filling the coordination sites not saturated by bridging

hydroxides. As means of providing context, several examples of cluster compounds containing mixtures of octahedral and tetrahedral metals are mentioned as well, particularly the much studied Keggin-Al_{13} ions.[2] The compounds discussed will not be limited solely to those isolated from aqueous solutions, as a significant number of recent compounds have been isolated from organic solutions as well.

Solid state structures are the focus of this review, and therefore the primary means of characterization is single-crystal X-ray diffraction (XRD). The necessity to isolate crystals suitable for single-crystal diffraction studies has in all likelihood limited the number of structures reported, as our own experience has shown that successful crystallization of these compounds can sometimes be elusive. While characterization of these compounds by solution means is often difficult or inconclusive, methods such as NMR, powder X-ray diffraction, mass spectrometry, and extended X-ray absorption fine-edge spectroscopy have been used to garner both solution phase and solid state data on metal hydroxide clusters.

Aluminum Clusters in the Environment

There are many reasons for interest in Group 13 hydroxide compounds. For example, aluminum is highly environmentally relevant, due to its high natural abundance (the most abundant metal in the biosphere) and geochemical diversity.[2] Aluminum itself has no known biological role, largely due to a lack of bioavailability of its natural mineral forms.[9] However, as human activity has begun to produce large quantities of

bioavailable aluminum, various environmental problems such as poisoning of fish in lakes and the dreaded "Waldsterben" in forests exposed to acid rain have been attributed to aluminum.[9,10] In fact, several neutral Al(III) complexes with organic ligands have shown to have much higher toxicity than inorganic aluminum salts.[11] Biological effects have been attributed to enzyme inhibition, nucleotide destruction, or mineral formation. To better understand these biological effects, research on aluminum aggregates has examined the similar hydrolytic behavior of iron and aluminum, seeking to establish whether Al(III) might be incorporated into biological systems through similar pathways to Fe(III). For instance, can aluminum be incorporated into biomolecules like ferritin?[9] Synthetic aluminum complexes may also provide insight into iron-containing metalloenzymes.

Also of environmental relevance, aluminum sols have been shown to transport heavy metal ions out of mining areas. The sols bind to heavy metal ions and the complexes remain soluble due to the acidic conditions of the mining areas. As the sol-containing water leaves mining areas, the pH rises upon contact with native waters, rendering the aluminum complexes insoluble, and flocs precipitate out of solution with the heavy metal ions.[12] A similar process is used in a positive light to sequester heavy metals and other contaminants from drinking water supplies where precipitates are easily filtered off and removed.[13] Beyond their use in water purification, aluminum compounds have found applications in many other areas as well. Examples include the formation of ceramics (through clay pillaring agents) and antiperspirants where aluminum chloride salts are a common ingredient.[14]

Beyond these direct applications of aluminum complexes, another body of work has focused on the use of synthetic aluminum compounds as mineral mimics.[2] The structure and reactivity of many minerals is poorly understood because the surface of bulk samples is often difficult to characterize.[2] The use of synthetic small molecule analogues for these structures enables the prediction of some of the natural processes taking place at the surface of natural minerals, such as exchange of water ligands and oxygen atoms. The controlled nature of a laboratory and the smaller sizes of the cluster compounds can provide a clearer understanding of the more complicated processes in nature. One compound that fits into all of the above categories is the Keggin-Al_{13} structure.[15] It has been used as a sequestration agent, clay pillaring agent, and mineral mimic. It has even been shown to form naturally in aqueous environments where it can be prevalent in high concentrations.[12] In this compound, the central tetrahedral aluminum metal ion can be exchanged, with Ga or Ge taking its place.[13,15-18] But aside from this prominent example, few Group 13 oxo/hydroxo compounds are known, with even fewer Group 13 hydroxides.

Gallium and Indium

Moving down the group, gallium and indium are far less abundant than aluminum and have been used and studied to a lesser extent. However, both have seen increasing use in the semiconductor industry, where they are key components in III/V semiconductors. Additionally, some state of the art solar cell technology utilizes copper-

indium-gallium selenide (CIGS) as the photovoltaic layer. Devices using this technology currently show great promise for photovoltaic efficiency, with systems demonstrating nearly 20% efficiency having been prepared.[19] Similarly, the oxides of these materials, such as gallium oxide, indium oxide, and indium-gallium oxide, have been shown to be effective components of amorphous thin film semiconductors.[20,21] Recent efforts have demonstrated the use of Group 13 hydroxide clusters as precursors for materials of this type.[21] A better understanding of the chemistry of hydroxide compounds of gallium and indium may allow easier and more efficient isolation of important materials precursors.[20]

Inorganic Hydroxide Clusters

It has generally proven difficult to isolate purely inorganic Group 13 metal hydroxide clusters. As higher nuclearity structures form, high charge densities build up, and compounds are progressively less stable. In the case of a tridecameric Group 13 hydroxide cluster with formula "$M_{13}(OH)_{24}(H_2O)_{24}$", a +15 charge is present, compared to the Keggin-Al_{13} clusters with only a +7 charge (oxide ligands lessen the charge). Also, the water ligands that generally fill the coordination spheres of some metal ions in inorganic structures exchange rapidly in solution, decreasing the stability of the complexes in solution. Despite this, some lovely structures have been isolated, and are described in the following sections.

Inorganic Aluminum Clusters

The first example of an aluminum hydroxide cluster was a simple edge-shared dimer bridged by two hydroxides.[22] This structure, described in 1962 by Johansson, was proposed as a less basic salt intermediate compound to the larger Keggin-Al_{13}. The compound was isolated as both the sulfate and selenate salt, and each possesses four H_2O ligands that fill the coordination sites of the octahedral aluminum in addition to two waters of hydration to give structures of $[Al_2(\mu\text{-}OH)_2(H_2O)_8](SO_4)_2{\cdot}2H_2O$ and $[Al_2(\mu\text{-}OH)_2(H_2O)_8](SeO_4)_2{\cdot}2H_2O$ (Al_2). The sulfate was prepared by dissolving aluminum metal in sulfuric acid in the presence of a small amount of mercury catalyst, followed by filtration and crystallization of the resulting solution. The selenate was prepared by dissolving aluminum hydroxide in selenic acid. Individual clusters in each crystal structure hydrogen bond to each other through the oxygen atoms of the anions and water molecules. Following the isolation of this compound, it was another 36 years before another inorganic aluminum hydroxide oligomer was described in the solid state.[23]

The next larger oligomeric inorganic aluminum cluster to be isolated was $[Al_8(\mu_3\text{-}OH)_2(\mu\text{-}OH)_{12}(H_2O)_{18}](SO_4)_5{\cdot}16H_2O$ (Al_8).[24] This complex is isolated by Casey et al. in a similar manner to the Al_2 structure mentioned above, however, a longer crystallization time eventually yields Al_8 in low isolated yield. In this impressive complex, both edge-shared and corner-shared octahedra are found, with three different aluminum environments observed (Figure 1.1). The inner four aluminum ions are edge-sharing octahedra, bonded to each other through two μ_3-OH and two μ-OH bridging ligands (four total μ-OH ligands bridge the inner core). This inner core of four ions is bonded to four

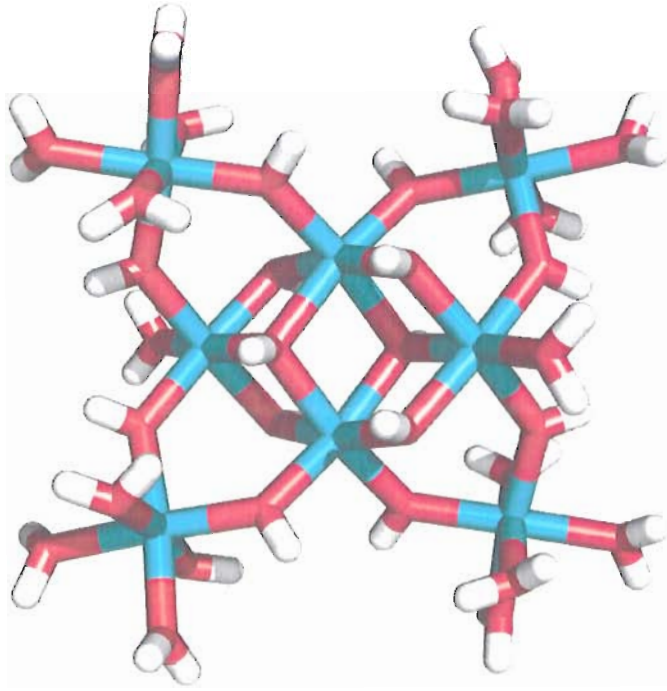


Figure 1.1. Depiction of the crystal structure of Al_8. An inner core of four edge-shared aluminum ions is found with four additional corner-shared aluminum ions capped by water ligands. Aluminum is teal, oxygen is red, and hydrogen is white; image generated with PyMol.

corner-shared aluminum ions through eight μ-OH bridges. The remaining coordination sites are filled by water ligands, one each on two of the edge-shared aluminum ions, and four water molecules bonded to each of the corner-shared aluminum ions. This structure is particularly interesting as it represents the only non-ligand supported intermediate between dimeric Al_2 and tridecameric M_{13} (M = Al or Ga) structures.

The next larger oligomer is the $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}]^{15+}$ (Al_{13}) cation, which has been isolated as both the Cl^- and NO_3^- salt (Figure 1.2).[23,25] The original isolation of this structure occurred when an aqueous solution of basic aluminum chloride

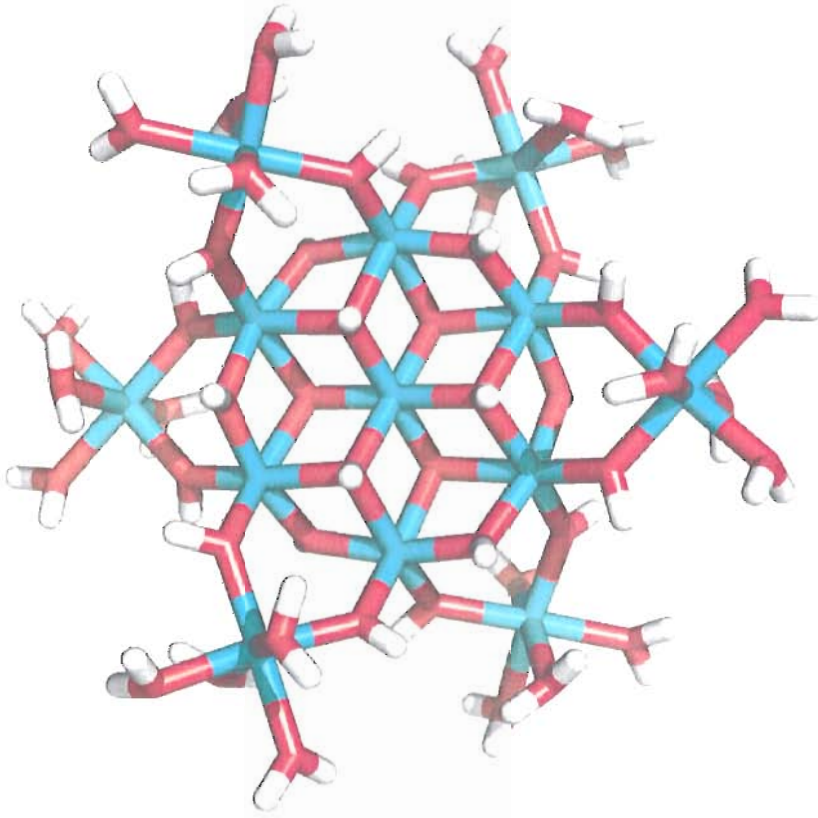


Figure 1.2. Structural depiction of the crystal structure of Al_{13}. This is the highest nuclearity inorganic aluminum hydroxide cluster. The heptameric central hydroxide core forms a planar center, while six additional aluminum ions are bridged by hydroxides and alternate positions above and below the central plane. Aluminum is teal, oxygen is red, and hydrogen is white; image generated with PyMol.

was slowly evaporated, affording crystalline solid that contained mostly large crystals of $AlCl_3 \cdot 6H_2O$ in addition to a small amount of the Al_{13} cluster. To synthesize this compound, $AlCl_3 \cdot 6H_2O$ was partially thermally decomposed at 180 °C in a whirling air stream. Crystals suitable for single crystal X-ray diffraction were isolated after four months of evaporation open to atmosphere.[23] This cluster had been previously suggested to exist based on powder X-ray diffraction data, but absolute assignment had not been

possible prior to the report by Seichter et al.[26] Initially, positions of all hydrogen atoms could not be established, so the location of hydroxide vs. water ligands was inconclusive. The authors used charge balance to draw their conclusions: the thirteen Al(III) ions have a +39 charge, which was countered by 15 Cl^- anions. This gave a remaining charge of +24, which is balanced by bridging hydroxide ligands. There are three different types of octahedral aluminum atoms present in this structure. The central aluminum atom is bonded to six μ_3-OH ligands. There are then six more aluminum atoms edge-shared with the central metal; each of these are bonded to two μ_3-OH bridges and four μ-OH bridges. Beyond the planar core of seven edge-shared aluminum atoms, there are six additional aluminum atoms, which are bonded to the core by two μ-OH bridges each. These outer shell metal ions alternate positions above and below the planar core of $Al_7(\mu_3\text{-}OH)_6(\mu\text{-}OH)_6$. The remaining coordination sites of the six exterior Al^{3+} ions are occupied by four water molecules per aluminum ion, giving a total of 24 coordinated water molecules, with thirteen additional waters of hydration present.[23]

The cluster isolated as the nitrate salt by Gatlin et al. is isostructural to that reported by Seichter et al., but the conditions for isolation are quite different.[25] $Al(NO_3)_3{\cdot}9H_2O$ was used as received, with no thermal decomposition procedure used. The aluminum salt was dissolved in methanol along with either di-*n*-butylnitrosamine or nitrosobenzene. A small amount of base (KOH, NaOH, NH_4OH, or $Al(OH)_3$) was added to the reaction vial as well. After several weeks, crystals of $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ were isolated. The crystalline product is generally a mixture containing other inorganic nitrate salts, such as $Al(NO_3)_3$. In the case where NH_4OH is

used as the base, an additional positive charge is present from a NH_4^+ cation with an additional NO_3^- present to balance the charge. This isolation represented the first intentional synthesis of this structure, and was achieved in a much faster time frame.

Inorganic Gallium Clusters

Moving down the periodic table, inorganic clusters of Ga(III) and In(III) become quite limited. The only example of an inorganic gallium hydroxide structure was isolated by two separate methods. The first isolation was by Rather et al. in a method similar to that of the second described Al_{13} synthesis: $Ga(NO_3)_3 \cdot nH_2O$ is dissolved in methanol with either nitrosobenzene or di-*n*-butylnitrosamine.[25,27] These solutions are then left to evaporate open to air for several weeks, at which point single-crystalline $[Ga_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (Ga_{13}) is isolated in 60% yield with nitrosobenzene and greater than 80% yield with di-*n*-butylnitrosamine (Figure 1.3).[21,25] This compound is isostructural with the Al_{13} hydroxide structure, but falls in a different crystallographic space group. It is rationalized that no base is required in this reaction because gallium is more Lewis acidic than aluminum (Ga(III) $pK_a = 2.6$, Al(III) $pK_a = 5.0$).[28] In the synthesis using nitrosobenzene, it was suspected that the nitroso functionality is oxidized to nitrobenzene, which works to consume nitrate and drive nucleation of the higher nuclearity species. However, experiments with di-*n*-butylnitrosamine revealed no evidence for the same oxidation (NMR and LC/MS suggest only starting material is present), while the clusters formed in higher yields. The use of di-*n*-butylnitrosamine

also allows isolation of Ga_{13} in much larger quantities, with gram-scale quantities synthesized within several weeks.[21]

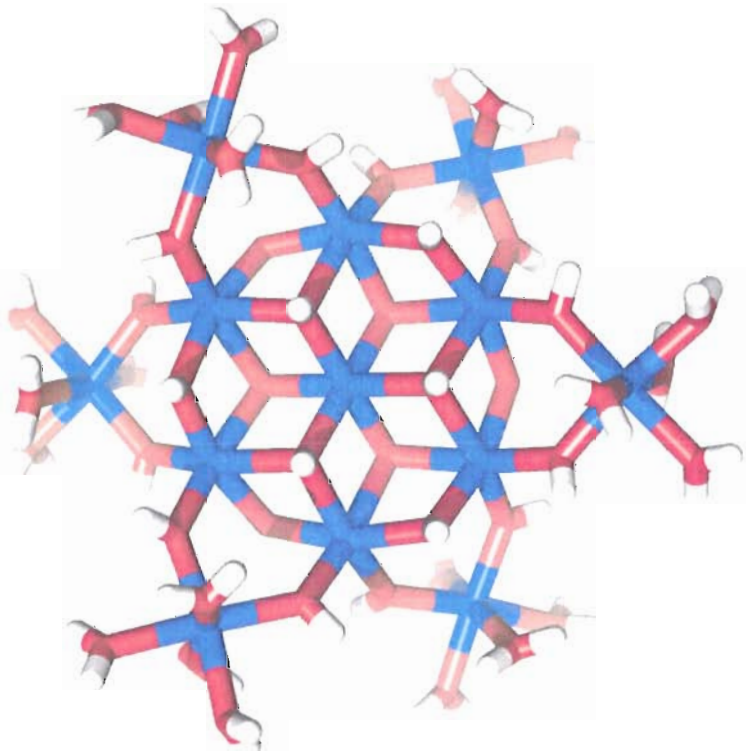


Figure 1.3. Structural depiction of the crystal structure of Ga_{13}. The tridecameric gallium hydroxide is isostructural with the Al_{13} cluster. There is the planar structural core with six additional gallium ions bridged to the core by hydroxides. These gallium atoms alternate positions above and below the plane of the core.

Nearly concurrently, Gerasko et al. reported the same Ga_{13} structure.[29] In this case, no organic nitroso compound was present. Instead, $Ga(NO_3)_3 \cdot 8H_2O$ was dissolved in water with cucurbit[6]uril. A small amount of pyridine as added dropwise to adjust the pH to 1.8. Without this step, no higher nuclearity clusters were isolated. Initially, a

wonderful higher nuclearity $[Ga_{32}(\mu_4\text{-}O)_{12}(\mu_3\text{-}O)_8(\mu\text{-}O)_7(\mu\text{-}OH)_{39}(H_2O)_{20}]^{3+}$ oxo/hydroxo compound crystallizes. The remaining liquid was separated and left for an additional two weeks, at which point more crystals of Ga_{32} were isolated along with crystals of Ga_{13}. The role of cucurbit[6]uril in the isolation of Ga_{13} is uncertain, and attempts to alter multiple reaction variables such as Ga(III) concentration, pH, and temperature failed to produce the cluster in its absence, so while the role of cucurbit[6]uril remains mysterious, it appears necessary nonetheless.

This cluster has also been isolated in the absence of nitroso compounds or cucurbit[6]uril. In several cases, I have isolated Ga_{13} simply from either methanolic solutions of $Ga(NO_3)_3$ or from methanolic solutions of $Ga(NO_3)_3$ with EtOAc added prior to solvent evaporation. In both cases, yields of the crystalline material appears similar to cases with di-*n*-butylnitrosamine present, however, the crystallization times are generally longer and product isolation is less consistent. Partially due to the wide range of conditions under which Ga_{13} has been isolated, its mechanism of formation (and the role of the nitroso additive) is still unknown. This observation also underscores a quizzical concept: why had Ga_{13} not been previously isolated? Perhaps prior attempts to recrystallize $Ga(NO_3)_3{\cdot}nH_2O$ have unknowingly produced Ga_{13} and it had just not been characterized as such.

Ligand Bound Hydroxide Clusters

Several of the above clusters have been isolated in ligand-supported forms as well. Ligand-supported clusters are often more readily isolated due to the mitigation of molecular charge by the organic ligands.[2] Inorganic clusters often build up extensive charge character, such as Ga_{13} and Al_{13} which each have +15 charges.[21,25,27] Complexation by organic ligands such as aminocarboxylates not only mitigates this charge, as in the case of a hydroxyethyliminodiacetic acid (H_3heidi) ligand which when complexed and deprotonated carries a -3 charge, but also fills the coordination sites on the peripheral metal ions. These would otherwise be occupied by water molecules which exchange much more rapidly. For these reasons, a larger variety of ligand-supported Group 13 hydroxides have been isolated.[9] Presence of ligands can also affect the shape and size of the species that form and crystallize by directing formation through ligand coordination geometry or steric bulk. With a wide variety of available ligands, it is perhaps not surprising that a wider variety of elegant compounds have been isolated by a number of research groups utilizing coordinating ligands.

Ligand Bound Aluminum Clusters

The simplest version of a ligand-supported aluminum structure is the aforementioned dimeric Al_2 structure.[22] They represent the largest variety of octahedral Group 13 hydroxide structures encountered, potentially because as higher nuclearities are generated, it becomes more difficult to walk the line between oxo/hydroxo and

oligomeric/polymeric species. This structural core has been observed in complexes isolated with several different ligand classes of varying coordination number. The structure with the greatest deviation from the inorganic dimer is that with heidi ligands reported by Heath et al., $[Al(heidi)(H_2O)]_2 \cdot 2H_2O$ (Al_2heidi_2, Figure 1.4).[9] In this case,

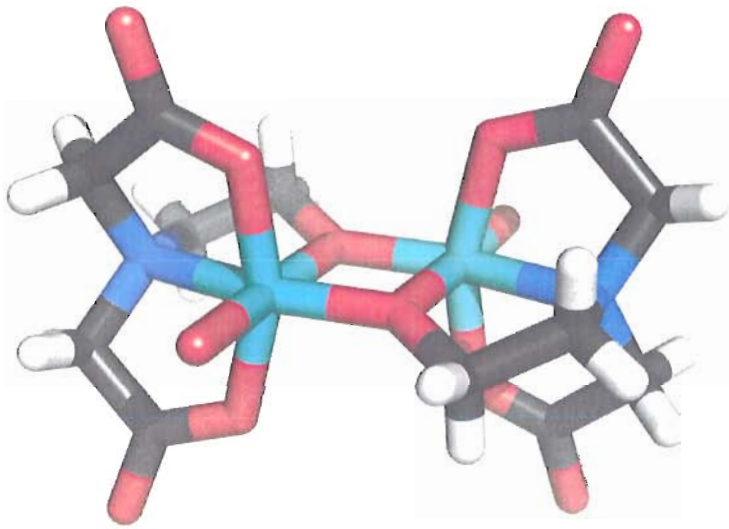


Figure 1.4. Structural depiction of the crystal structure of Al_2heidi_2. The heidi ligand can be seen binding to the aluminum atoms in place of water and hydroxide ligands. One water ligand per aluminum remains bound (shown without hydrogens). Aluminum is teal, oxygen is red, carbon is black, nitrogen is blue, and hydrogen is white; image generated with PyMol.

the hydroxyl bridges are actually replaced by the ethoxy groups of the heidi ligand. The aluminum ions bind to two ethoxy groups, two carboxylate oxygen atoms, one amino nitrogen atom, and one water ligand. This compound was isolated from a solution with a 2:1:4 ratio of H_3heidi:$Al(NO_3)_3 \cdot 9H_2O$:pyridine (pH = 4.3). Using $AlCl_3 \cdot 6H_2O$ in place of

$Al(NO_3)_3 \cdot 9H_2O$ affords the same compound with Cl^- counteranions. While this compound actually lacks any hydroxide bridges, it is included because of the structural similarity to the inorganic Al_2 structure, and because it represents a potential "intermediate" to higher order structures, as will be discussed in the case of ligand-supported gallium structures.[8,22]

Similar compounds, but with different carboxylate groups, have also been characterized in the solid state. In one case, nitrilotriacetic acid (H_3nta) is bound giving a $[Al(H_2O)_2][Al_2(\mu\text{-}OH)_2(nta)_2]OH \cdot 3H_2O$ formulation (Figure 1.5).[11,30] To isolate this compound, $Al(OH)_3$ was prepared and mixed with H_3nta in water with heating. Further treatment with acetone and ethanol gave a white powder, which when recrystallized from water by slow evaporation gave the described product.[11] H_3nta has been used as a detergent builder; its use has raised concerns about mobilization of toxic metal ions from deposits in lakes and rivers, driving research to determine what species it may be forming with metal ions.[11] Additionally, iminodiacetic acid (H_2ida) has given a similar planar dimeric dihydroxide structure, $[Al_2(\mu\text{-}OH)_2(H_2O)_2(ida)_2]$, but because ida only possesses two ethylcarboxylate functionalities, the resultant compound still has the bound water molecule found in the inorganic structure (Figure 1.5).[22,31,32] This compound was isolated by dissolving $Al(NO_3)_3 \cdot 9H_2O$, H_2ida, and NaOH in water in a 1:1:2 ratio. The solution was diluted with ethanol and evaporated over several weeks.[7]

Another example of a dimeric ligand-supported hydroxide structure was isolated by a less conventional method, obtained from non-polar organic solvents. A dimeric $[Al_2(\mu\text{-}OH)(\mu\text{-}CH_3CO_2)_2(CH_3CO_2CH_2CH_3)_5][AlCl_4]_3$ (Figure 1.6) compound was

isolated from a 1:2 ratio of ethyl acetate:$AlCl_3$ suspended in *n*-hexane.[33] The initial product was recrystallized in CH_2Cl_2 in the presence of moisture from the atmosphere

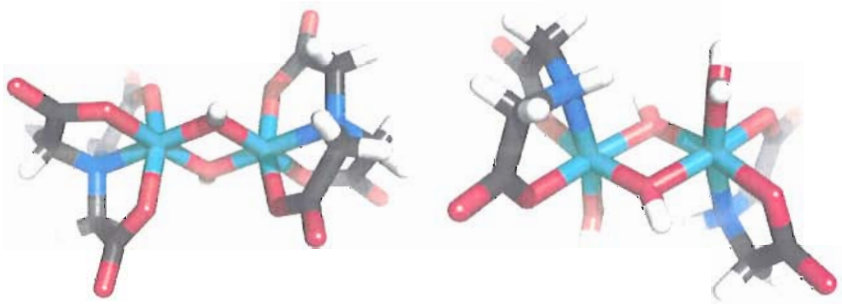


Figure 1.5. Depictions of the crystal structures of Al_2nta_2 and Al_2ida_2. In these structures, the ligands only have nitrogen and carboxylate coordinating groups. Because of this, there are no hydroxide ligands replaced, as with structures isolated with heidi ligands. Aluminum is teal, oxygen is red, carbon is black, nitrogen is blue, and hydrogen is white; image generated with PyMol.

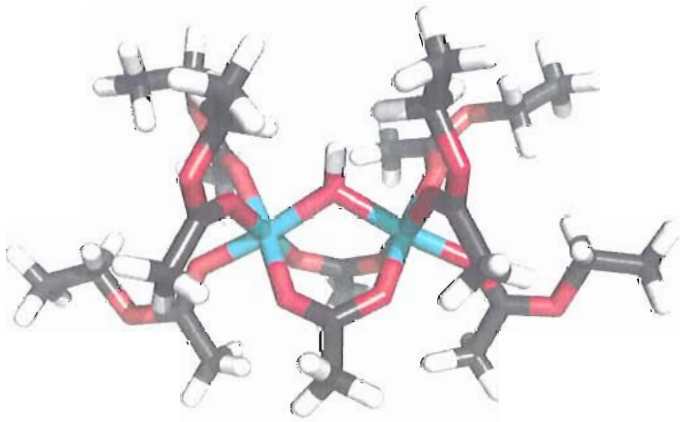


Figure 1.6. Dimeric aluminum species bound by ethyl acetate ligands. This structure has one hydroxide and two acetate bridging ligands. A total of six ethyl acetate ligands are bound to the aluminum atoms. Aluminum is teal, oxygen is red, carbon is black, and hydrogen is white; image generated with PyMol.

(originally introduced accidentally when solvent dissolved the grease used to seal the vessel). The colorless crystals with the stated formula were obtained more directly by exposing the recrystallization solution to air for one hour. This structure has potential interest in the area of polymerization catalysts, specifically for Ziegler-Natta, in order to better understand the interactions between ester molecules and the different catalyst components, in this case the organoaluminum cocatalysts.[33]

Another dimeric aluminum hydroxide compound is that formed by the reaction of $Al(NO_3)_3 \cdot 9H_2O$ with three equivalents of 2-(2'-hydroxyphenyl)-2-benzoxazole (Hhbo) and 3.5 equivalents of NaOH in an 80:1 mixture of MeOH:H_2O (Figure 1.7).[34] The phenolic group of the ligand is deprotonated and binds to the aluminum ion along with the nitrogen atom of the oxazoline. A total of four hbo ligands bind to the complex, along with two μ-OH bridges to give the formula $[Al(OH)(hbo)_2]_2 \cdot 4MeOH \cdot H_2O$ and a neutral compound. ^{27}Al NMR studies were used to show that the solution structure was the same as the solid state. Similar reactions with $Ga(NO_3)_3 \cdot nH_2O$ give different structures with no hydroxide bridges.[34] Interest in these compounds was stimulated by the desire to synthesize trivalent metal containing analogs of metalloenzymes containing polynuclear Fe(III) centers and carboxylato and/or hydroxo bridging ligands.[34]

The dimeric Al_2 core has also been isolated as a complex with another organic molecule: cucurbit[6]uril.[35] In this example, the structure of the inorganic compound remains intact ($[Al_2(\mu\text{-}OH)_2(H_2O)_8](NO_3)_4$) and forms an extended network with cucurbit[6]uril through hydrogen bonds only. The water ligands on the aluminum ions

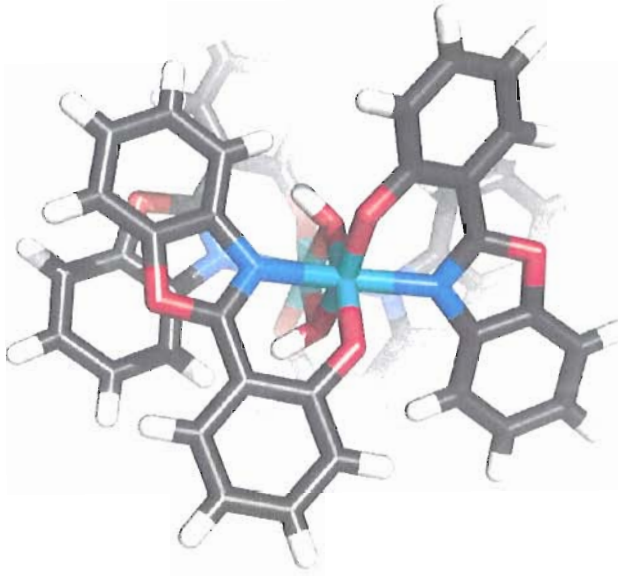


Figure 1.7. Dimeric aluminum hydroxide complex with hbo ligands. In this structure, a more rigid ligand is bound to aluminum. The aluminum atoms are bound to four oxygen atoms and two nitrogen atoms. Aluminum is teal, oxygen is red, carbon is black, nitrogen is blue, and hydrogen is white; image generated with PyMol.

hydrogen bond to the carbonyl oxygen atoms of the cucurbit[6]uril molecules. Each Al_2 dimer forms six hydrogen bonds to cucurbit[6]uril carbonyl oxygen atoms. The compound was isolated by evaporation of a solution of $Al(NO_3)_3 \cdot 9H_2O$ and cucurbit[6]uril, with pyridine added until a pH value of 3.1 was achieved. Pyridine molecules used to basicify the solution are bound as guests within the cavity of the cucurbit[6]uril host. This system forms an infinite chain of hydrogen bonded molecules. Waters of hydration, nitrate counteranions, and additional cucurbit[6]uril molecules are found between these hydrogen bonded chains.[35]

Beyond these varied cases of Al dimers, a trimeric aluminum complex with citrate has been isolated.[36] This compound, $(NH_4)_5[Al_3(cit)_3(\mu\text{-}OH)(H_2O)](NO_3)\cdot 6H_2O$ (Figure 1.8), is proposed as a possible species that forms in the interaction of aluminum with blood plasma. The structure was isolated by slow evaporation of an aqueous ammonia solution of aluminum nitrate and citrate. Each of the three aluminum ions in the molecule has a different coordination environment. The first is bonded only to citrate oxygen atoms, the second is bonded to five citrate oxygen atoms and a hydroxide bridge, and the third is bonded to four citrate oxygen atoms, one hydroxide bridge, and one water molecule. The space between the molecules is filled by a network of hydrogen bonded water molecules, ammonium cations, and a nitrate anion. The presence of an additional cation is similar to the synthesis of inorganic Al_{13} using NH_4OH as a base, where an extra NH_4^+ cation was present and charge balanced by an additional nitrate counteranion.[25]

Another aluminum citrate trimer was isolated by Malone et al.[37] The structure is far more symmetric than the previously discussed citrate trimer. Two Al(III) ions form a motif similar to that found in the Al(III) dimer species, with two μ-OH bridges shared between them. These aluminum ions are also coordinated by two carboxylate oxygen atoms from a citrate, an alkoxide from a citrate, and a water ligand. The third aluminum ion is coordinated through an alkoxide and carboxylate group from each of the two citrate molecules, in addition to two water ligands. The structure crystallizes as a double salt, with every two $[(Al_3(cit)_2(\mu\text{-}OH)_2(H_2O)_4]^-$ anions neutralized by one $[Al(H_2O)_6]^{3+}$ and one NO_3^-, giving a solid state complex with formula $[Al(H_2O)_6][(Al_3(cit)_2(\mu\text{-}OH)_2(H_2O)_4]_2(NO_3)\cdot 6H_2O$ (Figure 1.8).[37] This structure has two particular points of

interest: 1) the pH levels used for the synthesis (pH = 1.6) would normally give only monomeric citrate complexes, 2) the interesting appearance of monomeric hydrated aluminum ion. The second point is particularly interesting due to the presence of hydrolyzed Al(III) ions in the main section of the molecule, and is assumed to occur due to the excess of this species present at the low pH values of the synthesis.[37]

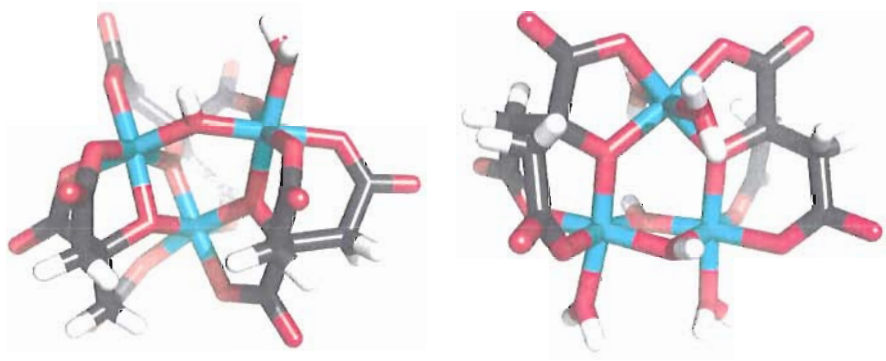


Figure 1.8. Depictions of two different trimeric structures with citrate. On the left, the structure only has one hydroxide bridge and one water ligand. The structure on the right has two hydroxide bridges and four bound water ligands. The structure reported by Malone et al.[37] is much more symmetric than the structure from Feng et al.[36] Aluminum is teal, oxygen is red, carbon is black, and hydrogen is white; image generated with PyMol.

A tetrameric aluminum complex with hydroxypropanediaminotetraacetic acid (H_5hpdta) has also been isolated, $(enH_2)[Al_4(\mu\text{-}OH)_4(hpdta)_2]\cdot 7.5H_2O$ (en = ethylenediamine).[7] This compound was synthesized by dissolving H_5hpdta and $AlCl_3\cdot 6H_2O$ in water, followed by slowly raising the pH to 5.8 through addition of ethylenediamine. Formation of this cluster species is thought to occur through a planar tetranuclear $M_4O(OH)(hpdta)_2(H_2O)_4^-$ species that forms upon the condensation of two

dimeric species. This species represents a fully dehydrated cluster (completely lacking water ligands, Figure 1.9) which is proposed to be particularly stable because H_2O ligands normally have a rapid exchange rate.[7] The aluminum atoms occupy the corners of a tetrahedron. Four edges of the tetrahedron are formed by hydroxide bridges, the other two by alkoxide groups from hpdta.

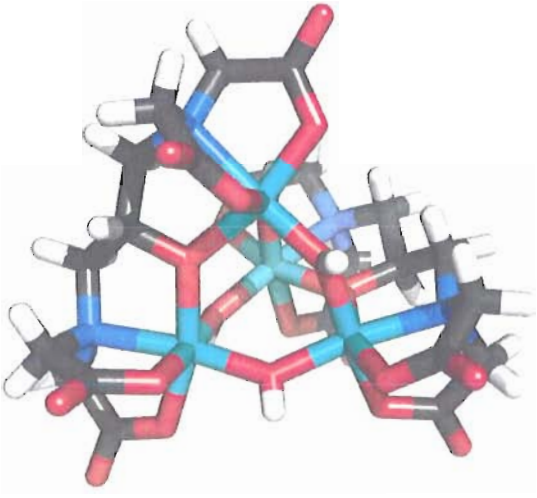


Figure 1.9. Tetrameric aluminum structure. The four aluminum atoms sit roughly on corners of a tetrahedron with the ligands forming the six edges of the tetrahedron. The hpdta ligand has the highest coordination number of the ligands encountered in a ligand-supported structure and each binds two different aluminum atoms. Aluminum is teal, oxygen is red, carbon is black, nitrogen is blue, and hydrogen is white; image generated with PyMol.

After the tetrameric species, there is a fairly large gap until the next ligand-bound aluminum oligomer, $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{12}(heidi)_6(H_2O)_6](NO_3)_3$ ($Al_{13}heidi_6$, Figure 1.10).[5] This compound was isolated in a similar procedure to Al_2heidi_2, with a 1:2 ratio of H_3heidi:$Al(NO_3)_3{\cdot}9H_2O$. Instead of pyridine to adjust the pH (pH 5 gives the best

yields), 1 M NaOH was used. As with Al_2heidi_2, using $AlCl_3 \cdot 6H_2O$ in place of $Al(NO_3)_3 \cdot 9H_2O$ affords the same compound with Cl^- counteranions.[5] This complex has the same metal ion arrangement as the inorganic Al_{13} compound discussed earlier in this review.[23,25] A planar core of seven aluminum atoms is observed, all octahedral and

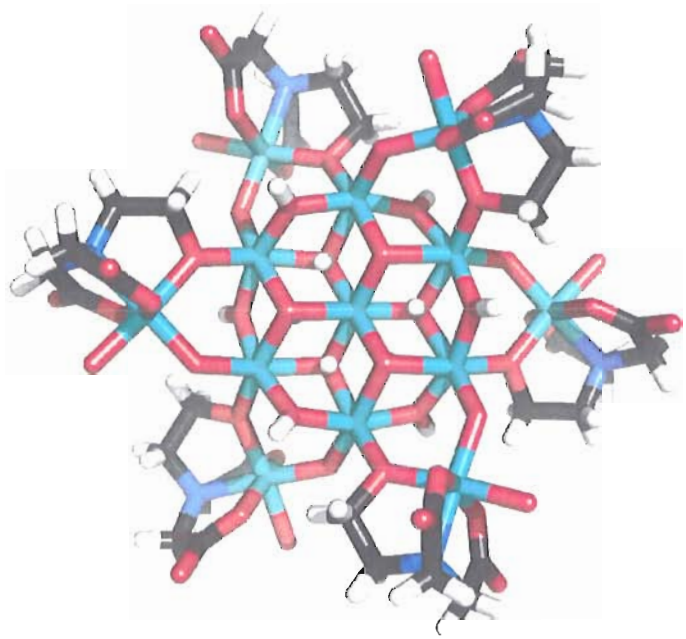


Figure 1.10. Tridecameric aluminum cluster bound by heidi ligands. This compound is roughly isostructural with the inorganic Al_{13} compound, with each heidi ligand replacing three water ligands and one hydroxide bridge between the outer aluminum atoms and the central core. Aluminum is teal, oxygen is red, carbon is black, nitrogen is blue, and hydrogen is white; image generated with PyMol.

bound to μ-OH ligands. Next are six additional aluminum atoms, alternating above and below the inner core of seven ions. These outer six aluminum ions are bound to the inner core through μ-OH bridges and the ethoxide group of the heidi ligand. The remaining four coordination sites of the octahedral ions are filled by two carboxylate groups, the

amino nitrogen of the heidi ligand, and one water molecule. The heidi ligands are again proposed to stabilize the structure against hydrolysis upon dilution. This compound has been examined as an alternative pillaring agent for clays to Keggin-Al_{13}, which are used as adsorptive media and catalysts. $Al_{13}heidi_6$ cations are inserted between layers of the clay and upon calcination yield oxide pillars that have two-dimensional porosity, achieving surface area values up to 350 m^2g^{-1}.[6,38]

Ligand Bound Gallium Clusters

Moving down the group to gallium, an isostructural compound to the Al_2heidi_2 compound has been isolated by Goodwin et al., $[Ga(heidi)(H_2O)]_2$ (Ga_2heidi_2, Figure 1.11).[8] This structure possesses the same geometry and morphology of the Al_2heidi_2 structure, with gallium ions replacing the aluminum ions. Isolation is achieved by reaction of a 2:1:8 ratio of hydrated $Ga(NO_3)_3$, H_3heidi, and pyridine in aqueous solution. Evaporation of this solution yields the Ga_2heidi_2 complex, as well as $[Ga_8(\mu_3\text{-}OH)_2(\mu\text{-}OH)_8(heidi)_4(H_2O)_4(C_5H_5N)_2]^{2+}$, described in the next paragraph. If a 1:1 ratio of gallium nitrate and H_3heidi are dissolved with two equivalents of sodium hydroxide, Ga_2heidi_2 is isolated exclusively.

The $[Ga_8(\mu_3\text{-}OH)_2(\mu\text{-}OH)_8(heidi)_4(H_2O)_4(C_5H_5N)_2]^{2+}$ (Ga_8heidi_4, Figure 1.12) structure was isolated along with the Ga_2heidi_2 compound. This is a fascinating example of multiple discrete compounds being isolated from the same reaction mixture. Similar to the inorganic Al_8 structure isolated by Casey et al., Ga_8heidi_4 contains a tetrameric core

of edge-shared gallium ions, $[Ga_4(\mu_3\text{-}OH)_2(\mu\text{-}OH)_2]^{6+}$, which is bound to four corner-shared $[Ga(heidi)(H_2O)]^+$ units. Each heidi ligand replaces three water ligands on the corner-shared gallium atoms (when compared to the inorganic Al_8 structure) and a μ-OH ligand between the edge-shared ions and corner-shared core.[24] Two pyridine ligands also replace two water ligands that are bound to the edge-shared Al(III) ions in the Al_8 structure (Figure 1.1 and 1.12).

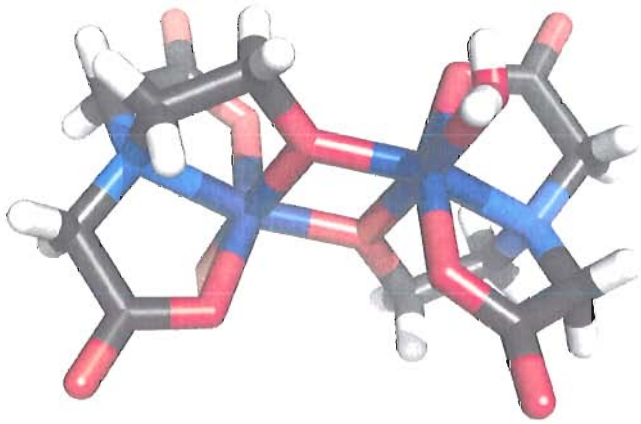


Figure 1.11. Dimeric gallium compound bound by heidi ligands. Gallium is bound by heidi ligands in the same manner as the Al_2heidi compound. The ethoxide group replaces a hydroxide bridge, with three additional coordination sites filled by the heidi ligand. Gallium is dark blue, oxygen is red, carbon is black, nitrogen is blue, and hydrogen is white; image generated with PyMol.

After the initial isolation of the Ga_8heidi_4 structure, fascinating behavior was observed.[8] From the solid state, the compound redissolves and within six weeks recrystallized as needles of a higher nuclearity, $[Ga_{13}(heidi)_6(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{12}(H_2O)_6]^{3+}$ ($Ga_{13}heidi_6$) complex (Figure 1.13). This compound is isostructural with the $Al_{13}heidi_6$

compound, featuring the same planar core of seven metals with an additional ring of six gallium ions alternating above and below the plane formed by the inner seven. The heidi ligand has the same connectivity as well, with three water ligands replaced by two

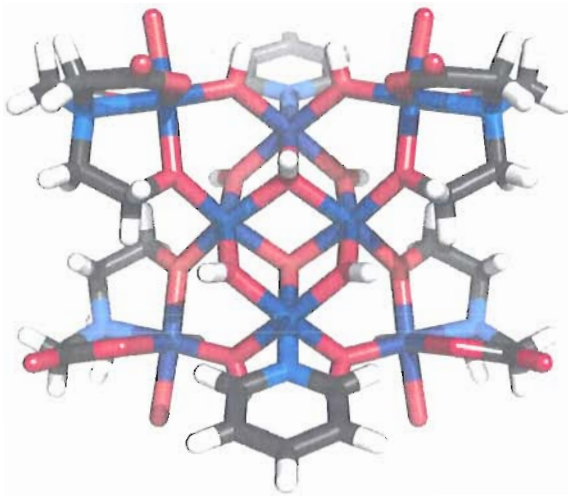


Figure 1.12. Heidi and pyridine ligands bound to an octameric gallium hydroxide core. In the Ga_8heidi_4 complex, a similar motif is seen where heidi replaces three water molecules and one hydroxide bridge as compared to the inorganic Al_8 compound. The central core is composed of four edge-shared gallium octahedra. Gallium is dark blue, oxygen is red, carbon is black, nitrogen is blue, and hydrogen is white; image generated with PyMol.

carboxylate groups and the amino nitrogen. The ethoxide ligand again replaces the μ-OH bridges in between the core and outer shell. The compound can also be isolated directly from a 3:1 ratio of H_3heidi:$Ga(NO_3)_3$ by adjusting the pH of the solution to 5 with pyridine. This represents an interesting reversal of base addition from the Al_2heidi_2 and

$Al_{13}heidi_6$ structures where pyridine is used for the dimeric structure and NaOH for the tridecameric structure.

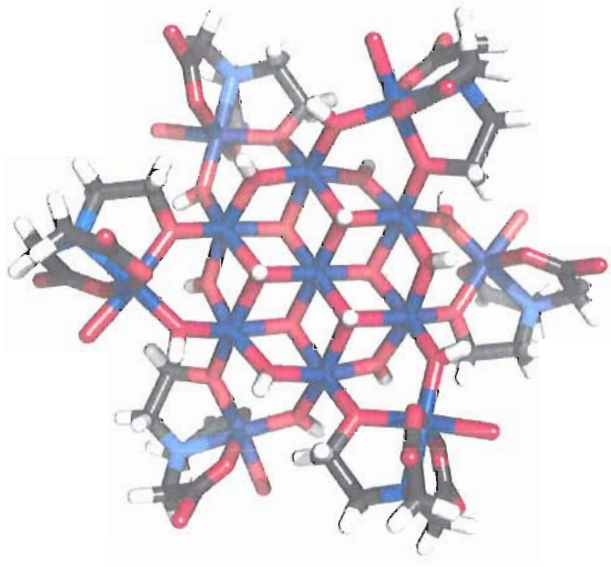


Figure 1.13. The highest nuclearity gallium hydroxide ligand-supported structure. All six exterior gallium atoms are bound to heidi ligands, with the same coordination mode as seen previously. The central planar heptameric core remains intact. Gallium is dark blue, oxygen is red, carbon is black, nitrogen is blue, and hydrogen is white; image generated with PyMol.

This report was unique because three different, but related clusters were isolated from the same reaction mixture. This was important because it allowed formation of the first conclusions about the growth of these cluster compounds based on observed "intermediates", Ga_2heidi_2 and Ga_8heidi_4.[8] It had previously been suggested that a seven metal core was a likely intermediate on the way to higher nuclearity structures such as the tridecameric clusters, but in conjunction with the inorganic Al_8 compound, it seems likely

that in the case of Group 13 metals, this complete shell of the brucite lattice does not need to form prior to addition of other metal ions. To isolate structures of increasing nuclearity with no pH alteration is a fascinating and unexpected result.

Ligand Bound Indium Clusters

I have come across only two examples of indium hydroxide compounds, both slight variations of a tetrameric structural core. In these tetrameric $[(tacn)_4In_4(\mu\text{-}OH)_6](S_2O_6)_3 \cdot 4H_2O$ and $[(tacn)_4In_4(\mu\text{-}OH)_6](ClO_4)_6 \cdot 6H_2O$ compounds (tacn = 1,4,7-triazacyclononane), the indium atoms occupy the corners of a tetrahedron and the six hydroxide bridges lie above the edges of the tetrahedron.[39] Each indium atom is bound to three hydroxide bridges and three nitrogen atoms. There are waters of crystallization as well, which have significant mobility in the structure at room temperature. These compounds were isolated from aqueous solutions of $InBr_3$, NaOH (pH ~ 8), and the corresponding sodium salts. Colorless crystals of the product form in good yields. The authors reported that other counterions can be used as well, suggesting perhaps that with indium compounds, the counterion may play a smaller role, unlike gallium compounds which have usually used NO_3^- counteranions.

Heterometallic Clusters

Beyond the homometallic inorganic and ligand-supported clusters described above, our group has been able to isolate a series of inorganic heterometallic clusters.[40] These clusters are the first of their kind. As mentioned in the introduction, previous reports have described the substitution of the central tetrahedral metal in Keggin-Al_{13} compounds (with either Ga or Ge) but there are no reports of heterometallic Group 13 compounds with all hydroxide bridges and all octahedral metals.[16,17] The initial compounds of this type we were able to isolate contained mixtures of gallium and indium. We isolated and characterized a series of six compounds where indium takes the place of gallium in the outer shell sites of the original Ga_{13} cluster ($Ga_{7+x}In_{6-x}$, $x = 0 - 5$). These clusters possess the same structural motif observed in the Ga_{13} compound with a planar core of seven Ga(III) atoms always maintained (Figure 1.14).[27,40] The same synthetic methods used to isolate Ga_{13} were utilized to isolate these Ga/In heterometallic compounds. Instead of starting with a solution containing only $Ga(NO_3)_3$ as with the Ga_{13} synthesis, various ratios of $Ga(NO_3)_3$ and $In(NO_3)_3$ are dissolved in methanol with di-*n*-butylnitrosamine. No pH adjustment is performed, and solutions are evaporated open to atmosphere. In the extremes, a 1:12 ratio of $Ga(NO_3)_3$:$In(NO_3)_3$ gives Ga_7In_6 and a 5:1 ratio of $Ga(NO_3)_3$:$In(NO_3)_3$ gives $Ga_{12}In$. With larger quantities of these compounds available, the Ga_7In_6 compound has been used as a precursor material for solution-processed amorphous indium-gallium oxide thin films.[21,40]

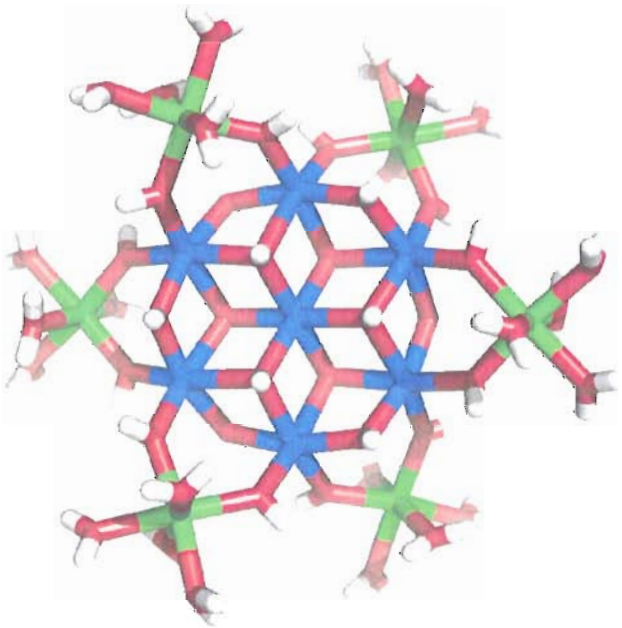


Figure 1.14. Heterometallic compound consisting of gallium and indium atoms. The heterometallic Group 13 hydroxide structures are isostructural with the Al_{13} and Ga_{13} homometallic compounds. Indium atoms are found in the exterior, corner-shared positions. Gallium is blue, indium is green, oxygen is red, and hydrogen is white; image generated with PyMol.

In addition to the heterometallic Ga/In hydroxide clusters, we also isolated several heterometallic Al/In hydroxide clusters. These structures are again isostructural to the previously described inorganic tridecameric structures. In this case, as with the Al_{13} synthesis, base addition is required to successfully isolate crystalline product of the clusters. As with the other heterometallic clusters, substitution of indium for aluminum only takes place at the exterior metal sites. Unlike the Ga/In compounds however, only two heterometallic Al/In compounds have been isolated, Al_8In_5 and Al_9In_4. For Al_8In_5,

$Al(NO_3)_3$:$In(NO_3)_3$ ratios of 6:7 and 7:6 both afforded the compound. For Al_9In_4, 9:4 and 8:5 ratios of $Al(NO_3)_3$:$In(NO_3)_3$ were utilized to isolate the compound.

Discussion

Summarizing the structures presented in this review, there are three primary observed structure types for purely inorganic hydroxide compounds: dimeric, octameric, and tridecameric. When ligand-supported compounds are considered, there is wider structural variety: dimers, trimers, tetramers, octamers, and tridecamers have all been observed bound by a variety of ligands (Figure 1.15), and when structures with some oxo bridges are considered, even more structure types are observed.[7,41] Most of the described compounds were isolated from aqueous solutions, but a wide variety of recently reported tridecamers have been isolated from methanolic solutions, suggesting this may be an avenue for other researchers to explore. It is proposed that the use of methanol may help attenuate the hydrolysis of the metal ions and prevent precipitation of unspecified oligomeric products.[42]

It has been suggested that the formation of these hydroxide clusters follows the formation of a brucite type lattice.[2,8] Brucite, $Mg(OH)_2$, forms planar sheets of hydroxide ligands with octahedral holes.[8] In the case of many of the higher nuclearity clusters discussed in this review, the compounds are partial sections of a brucite lattice with aluminum, gallium, or indium filling the octahedral holes. Group 13 hydroxide structures with a brucite structure type have not been observed with nuclearity above thirteen metal

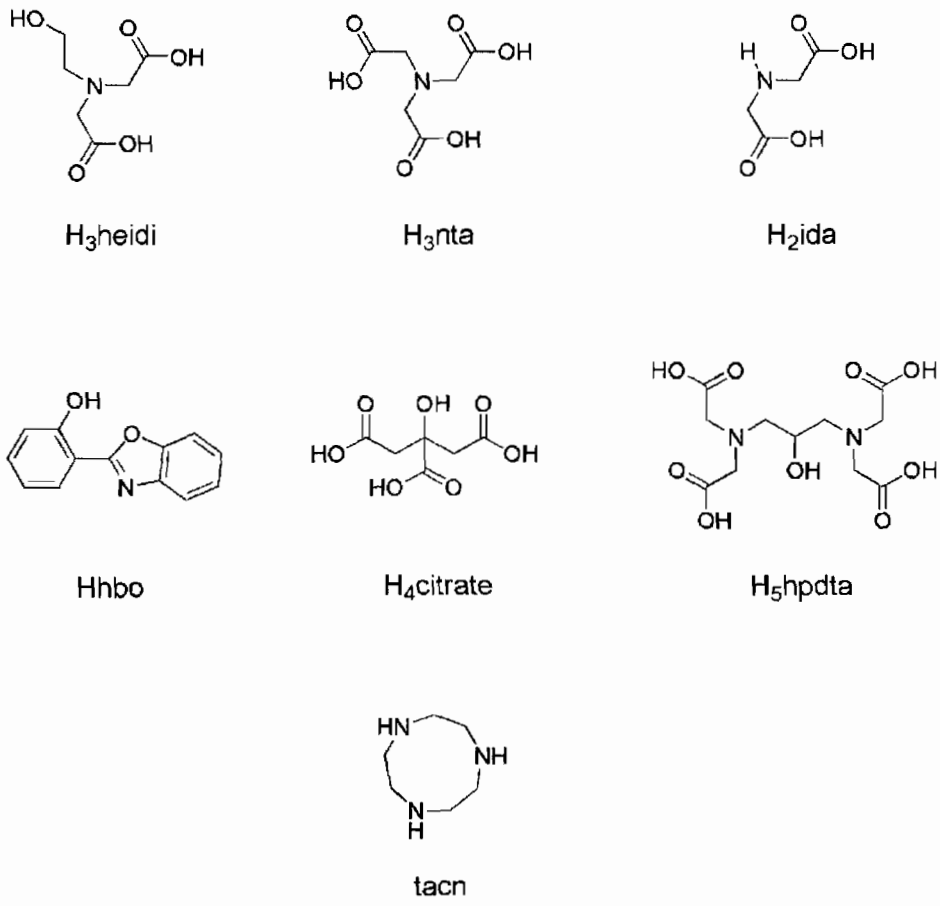


Figure 1.15. Summary of ligands in ligand-supported compounds. As stated, amino carboxylates are often used as coordinating ligands for Group 13 metal hydroxide structures. Compounds containing Hhbo, H_4citrate, and tacn were also summarized.

ions (though there are examples of higher nuclearity compounds with partial brucite lattice structure containing oxo ligands), while in the case of Mn and Fe, higher nuclearity brucite type structures have been isolated, such as Mn_{19} and Fe_{19}.[7] The closest example to such a structure with Group 13 is the elegant $[Al_{15}(\mu\text{-}O)_4(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{14}(hpdta)_4]^{3-}$ cluster isolated by Powell et al., where the exterior eight metal ions no longer lie in a plane and four of the exterior hydroxide bridges have been deprotonated to

form oxide bridges.[41] By analyzing the known structures, we can gain a better understanding of the stable fragments and intermediate speciation along the path to higher nuclearity brucite type structures.

What we ourselves, and we assume others, have learned through the years of working with Group 13 metal hydroxide compounds is that you can never fully predict their behavior. While the heterometallic Ga/In structures form quite readily, we have yet to isolate any strictly indium-based structure, the closest being an indium acetate hydroxide 1-D chain structure, which could to some extent be considered a ligand-supported structure, though was excluded because of its infinite nature.[43] Indium seems more likely to form extended structures such as those observed with benzene carboxylate ligands, many examples of which exist in the literature.[44-48] Similarly, while many ligand-supported Fe(III) complexes have been isolated, we have yet to isolate any inorganic Fe(III) hydroxide compounds, certainly not for lack of trying.

In considering Fe(III) and Mn(II or III) compounds, ligand-supported versions of Fe_7 and Mn_7 cores have been isolated.[49,50] Heptameric cores of this type were thought to be the building block for larger structures such as the tridecameric Ga_{13} and Al_{13}. However, with Group 13 metals, octameric structures are the highest nuclearity structures observed prior to the tridecameric compounds (with no reports of heptameric Group 13 hydroxides), suggesting these may instead be intermediates to the larger structures. Goodwin et al. provided structural evidence for this through their report of Ga_8heidi_4 redissolving and recrystallizing as $Ga_{13}heidi_6$.[8] In regard to the heidi ligand, it is also interesting to note that in all ligand-supported structures where heidi ligands are present,

the same binding motif is observed, with the ethoxy group of the heidi ligand replacing a hydroxide bridge while an H_2O ligand remains. It seems that alkoxide ligands will take the place of the hydroxide bridges, while carboxylate groups bind in place of water ligands (as compared to the inorganic congeners). This more firm structural incorporation of the heidi ligand suggests that it may be difficult to achieve post-synthetic ligand exchange for such a ligand onto inorganic compounds, such as Ga_{13}.

Comparing reports summarized in this review, a number of additional "missing" structures can be highlighted as potential synthetic targets, such as the inorganic Ga_8 isomer of inorganic Al_8, the Al isomer of Ga_8heidi_4, and gallium dimers, trimers, and tetramers isostructural to the aluminum structures summarized here.[5,7,8,24,30] Many potential indium compounds may be worth pursuing as well, as compounds containing indium remain quite limited. The "bewildering variety of behavior" of these compounds can be both inspirational and infuriating; it seems sometimes certain compounds exist on a knife's edge of pH range, and before you know, slip away into the abyss of chemical speciation (or the amorphous precipitate on the bottom of your flask).

Bridge to Chapter II

The following chapters summarize the work I have been involved with in the area of tridecameric Group 13 hydroxide structures, such as homometallic Al_{13} and Ga_{13} and a host of heterometallic compounds. In Chapter II, the reader will be treated to a thorough discussion of the tridecameric cluster at the top of the chart, Al_{13}.

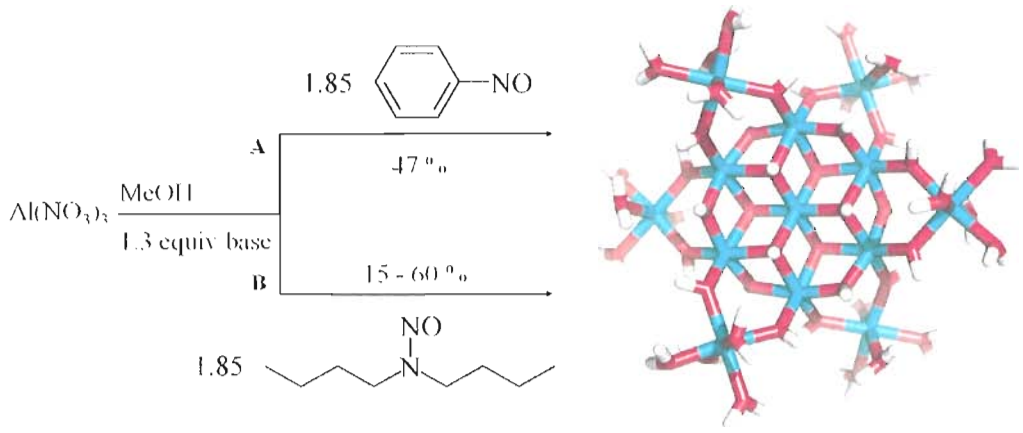
CHAPTER II

FACILE SYNTHESIS OF THE TRIDECAMERIC Al_{13} NANOCLUSTER $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$

Introduction

This chapter discusses the synthesis and isolation of a tridecameric aluminum hydroxide cluster. This work represents the first intentional synthesis of this compound. I contributed to this work through the development of the synthetic method utilizing an alternative reagent, di-*n*-butylnitrosamine, which allowed superior yields and easier isolation of the title compound and has enabled much of the progress detailed in the following chapters. I also contributed to the writing of drafts and extensive editorial work. Dr. Jason T. Gatlin initially isolated the compound and was the primary author of the initial draft of the manuscript. Dr. David MacInnes was a visiting faculty member from Guilford College who worked on yield determinations and some editorial aspects. Dr. Lev N. Zakharov was responsible for collecting most, and solving all, of the X-ray crystal structures presented in this chapter, and wrote the X-ray details. Prof. Darren W. Johnson was the principle investigator for this work and provided editorial assistance. This work was published in volume 47 of *Inorganic Chemistry*, a publication of the American Chemical Society, in January 2008.[1]

Aluminum is the third most abundant element and the most abundant metal in the earth's crust, found in many minerals and ores. Aluminum complexes are widespread in our environment, often occurring in natural waters and clays as hydrated salts or clusters containing multiple aluminum ions held together through various bridging groups.[2-11] Despite the widespread prevalence of natural aqueous aluminum oligomers, relatively few have been synthesized on a preparative scale and analyzed by single-crystal X-ray diffraction (XRD).[2] Furthermore, existing syntheses of many of these inorganic aqueous clusters suffer from long reaction times and/or poor yields (in cases where yields have even been reported), hampering efforts to study the applications and bulk properties of these materials.[2,5,6,9,12] In this chapter, we report facile syntheses that yield larger-scale amounts of single crystals of inorganic $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}]^{15+}$ (**Al$_{13}$**) clusters with various counterions (Scheme 2.1).



Scheme 2.1. Synthetic scheme depicting the synthetic preparation of the Al$_{13}$ compound. Two different synthetic routes can be followed, either **A**, utilizing nitrosobenzene as the organic additive, or route **B**, utilizing di-*n*-butylnitrosamine. In either case, base must be added to the reaction in order to isolate the desired compound.

Related Group 13 Hydroxide Clusters

Oligomeric aluminum clusters are found in two general structure types: (1) structures similar to the ε-Keggin tridecameric clusters composed of a central tetrahedral metal ion surrounded by edge-shared octahedral AlO_6 units[2,3,13-15] and (2) clusters comprised entirely of octahedrally coordinated aluminum cations (such as "flat" $\mathbf{Al_{13}}$; Figure 2.1). Only a few reports of the latter class of clusters exist and many of these are ligand-supported compounds.[2,5,7-9,12] We report the synthesis of two slightly structurally different versions of the purely inorganic salt $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ ($\mathbf{Al_{13}}$), a member of the latter class of octahedral polycations. The synthesis of these

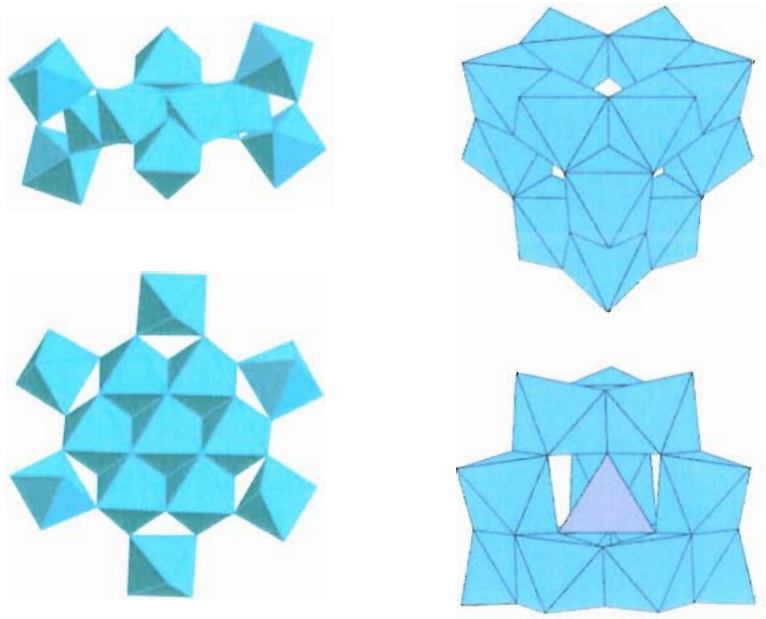


Figure 2.1. Comparison figure of the "flat" Al_{13} and ε-Keggin Al_{13}. The two images on the left depict the "flat" $\mathbf{Al_{13}}$ with all octahedral metal ions while the images on the right depict the ε-Keggin-Al_{13} ion which has a central tetrahedral metal and is more spherical in nature than the disc-like structure formed by the "flat" $\mathbf{Al_{13}}$.

purely inorganic aluminum salts has been reported as difficult and often highly elusive.[2] The synthesis reported herein proceeds in reasonable isolated yields under ambient conditions and in larger amounts than previously isolated. The synthesis is similar to the routes for the $[Ga_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (**Ga_{13}**) congener which are reported in the literature and described in Chapter III.[16]

Synthetic Procedure for Tridecameric Al Hydroxide

Two recent syntheses of the structure **Ga_{13}** were independently reported using gallium nitrate and an organic additive (nitrosobenzene or cucurbit[6]uril).[16,17] We developed a simple conversion of $Ga(NO_3)_3$ into the **Ga_{13}** nanocluster that proceeds in the presence of nitrosobenzene. In this reaction, nitrosobenzene is suspected to act as a scavenger for the nitrate counterions, in effect forcing the Ga(III) cations to form a higher-nuclearity species. The stoichiometry for the process involves the reaction of 13 equivalents of $Ga(NO_3)_3$ with 24 equivalents of nitrosobenzene to prepare 1 equivalent of **Ga_{13}** in limited quantities and up to 65 % yield.[16] A related **Al_{13}** core structure had been reported previously: structures supported by both exogenous aminocarboxylate ligands and the inorganic chloride salt are known.[5,9] However, the synthesis of the chloride salt suffers from a four and a half month preparation, and only data on a single crystal were reported.[9] Therefore, we sought to apply our synthetic strategy using organic nitroso compounds to prepare the analogous **Al_{13}** structures. The method used to form **Ga_{13}** can be modified to form the related tridecameric aluminum cluster by a key modification: the

reaction to form **Al_{13}** requires the addition of 1.3 equivalents of base, presumably a result of the increased pK_a of hydrated aluminum complexes over gallium (Scheme 2.1).[18] Single crystals of **Al_{13}** were isolated in unoptimized yields of up to ~40 % in two weeks from a methanolic solution of aluminum(III) nitrate nonahydrate, KOH, and nitrosobenzene (longer crystallization times often afford higher yields). A similar procedure using di-*n*-butylnitrosamine in place of nitrosobenzene also affords **Al_{13}** in reasonable yields (15-60 %, depending on the base) and provides for a far easier workup because crystals are isolated from the remaining liquid nitrosamine rather than the tarry sludge left over from the nitrosobenzene procedure (Figure 2.2). We have similarly found that di-*n*-butylnitrosamine provides higher yields of the related **Ga_{13}** complex.[19]

*Synthesis of $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (**Al_{13}**) by route **A** (Scheme 2.1).* Methanolic solutions of aluminum nitrate nonahydrate (0.50 g, 1.33 mmol, 13 equiv. in 5 mL MeOH) and nitrosobenzene (0.303 g, 2.82 mmol, 24 equiv. in 5 mL MeOH) were mixed together and 1.3 equivalents of KOH were added. The mixture was evaporated slowly at room temperature over 4-8 days in a scintillation vial covered with tissue paper, yielding a dark thick oil embedded with large single crystals of **Al_{13}**, which were isolated in ~40 % yield (with respect to aluminum nitrate).

*Synthesis of $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (**Al_{13}**) and $NH_4[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{16}$ (**$Al_{13}{\cdot}NH_4NO_3$**) by route **B** (Scheme 2.1).* Aluminum nitrate nonahydrate (0.25 g, 0.667 mmol, 13 equiv.) was dissolved in 2.5 mL of MeOH and di-*n*-butylnitrosamine (0.34 g, 2.17 mmol, 42 equiv.) was added via a syringe. 2.5 mL of a 0.18 M KOH solution in MeOH was then added. This solution was thoroughly

mixed and left uncapped in a scintillation vial to evaporate over the course of several weeks. The remaining di-*n*-butylnitrosamine was then removed via a syringe and the solution was washed with ethyl acetate (3 × 4 mL), yielding a mixture of KNO_3 powder and single crystals of $\mathbf{Al_{13}}$, which was isolated in 60 % yield with respect to aluminum nitrate. This yield can be quite variable, as a number of other inorganic species crystallize as well. Alternate bases also effect the same transformation: NH_4OH (0.1 equivalent per equivalent of $Al(NO_3)_3$) provides a slightly different crystal form of the

Figure 2.2. Comparison of post-reaction conditions. On the left, a reaction containing nitrosobenzene as the organic additive is depicted; on the right is a reaction with di-*n*-butylnitrosamine, which is easily removed after the reaction, simplifying isolation of crystalline product.

cluster ($\mathbf{Al_{13}}$·$\mathbf{NH_4NO_3}$) in 15 % yield while 1.3 equivalents $Al(OH)_3$ combined with 11.7 equivalents of $Al(NO_3)_3$ provide $\mathbf{Al_{13}}$ in 15 % yield.

A drawback to the use of KOH as the base in this procedure is difficulty in isolation of pure $\mathbf{Al_{13}}$ from the powdery KNO_3 that presumably forms in the reaction as well. To avoid this time-consuming workup, we have successfully employed $Al(OH)_3$ and NH_4OH as alternate bases; all of the salts that form as byproducts are soluble in the final oily mixture from which the $\mathbf{Al_{13}}$ crystals are collected (route **B**, Scheme 2.1). However, careful pH control must be exercised, as too rapid or too extensive an increase in the pH results in the formation of insoluble $Al(OH)_3$.

Structural Description of Tridecameric Al Hydroxide

The single-crystal X-ray structure of the $\mathbf{Al_{13}}$ cluster reveals a planar centrosymmetrical Anderson-type "$Al(\mu_3\text{-}OH)_6Al_6(\mu\text{-}OH)_6$" core fragment surrounded by six aluminum ions.[20,21] The outer six aluminum atoms alternate above and below the planar core defined by the central seven metal ions, and they are coordinated by four terminal water ligands which fill their coordination sphere. Two μ-OH ligands connect each of these $Al(H_2O)_4$ fragments to the central core.[4,9,16] Two different single-crystal forms were obtained from the syntheses; however, the cluster cations are nearly identical. Using either KOH or $Al(OH)_3$ as the base provides ($\mathbf{Al_{13}}$·$9H_2O$), whereas route B with NH_4OH as the base provides ($\mathbf{Al_{13}}$·$\mathbf{NH_4NO_3}$·$10H_2O$), which has extra nitrate and ammonium counterions. The $\mathbf{Al_{13}}$ polycations determined in this work have a structure

similar to that of the $\mathbf{Ga_{13}}$ cluster cation in which all of the metal centers are octahedral (Figure 2.1, left).[16,17] In the solid phase, both of the $\mathbf{Al_{13}}$ clusters are centrosymmetric, in contrast to the $\bar{3}$ crystallographic symmetry of the $\mathbf{Ga_{13}}$ cluster cation, although the idealized symmetry of the $\mathbf{Al_{13}}$ cluster cations is close to $\bar{3}$. In $\mathbf{Al_{13}}$ and $\mathbf{Al_{13}{\cdot}NH_4NO_3}$, the clusters are surrounded by NO_3^- anions and solvent water molecules forming O-H···O hydrogen bonds (Figure 2.3). In the case of the crystals grown from the reaction using NH_4OH as the base, one molecule of NH_4^+ also co-crystallizes, necessitating the presence of an extra NO_3^- counterion for charge balance (resulting in 16 total). The hydrogen atoms of both the coordinating water molecules and the bridging μ-OH ligands are involved in numerous intermolecular hydrogen bonds. Similar hydrogen bonding is observed between clusters in $\mathbf{Ga_{13}}$ as well.

Conclusion

The method described in this chapter has allowed for the facile synthesis of two slightly different $\mathbf{Al_{13}}$ clusters, showing the generality of this strategy for preparing inorganic nanoclusters, producing both $\mathbf{Ga_{13}}$ and $\mathbf{Al_{13}}$ clusters so far. A procedure for synthesizing preparative amounts of clusters of this type may have utility to researchers in the field trying to use these clusters as discrete molecular mimics of minerals or as single-source precursors for thin film oxide materials.[2,3,19]

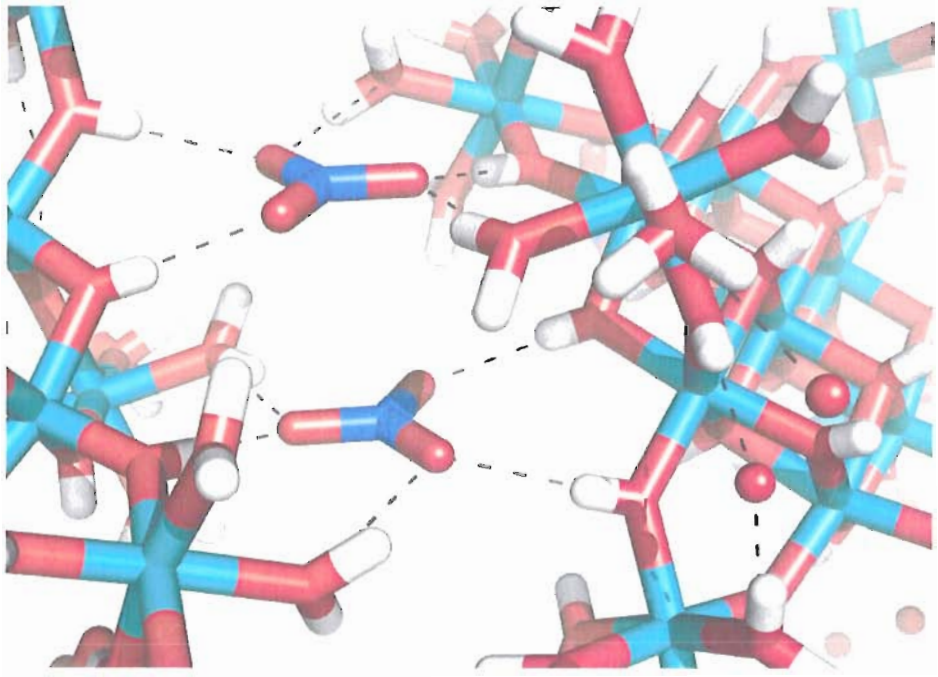


Figure 2.3. Depiction of hydrogen bonding between the nitrate counterions and the Al_{13} clusters. Nitrate counterions and water molecules form hydrogen bonds that bridge neighboring Al_{13} clusters in the solid state. Nitrate anions bond to both μ-OH bridges and water ligands bound to the exterior metal ions. Hydrogen bonds are indicated as dashed black lines. Interstitial water molecules are represented as spheres, with hydrogen atoms omitted. Image generated with PyMol.

Crystallographic Methods and Summary of Data

X-ray diffraction experiments were carried out on a Bruker Smart Apex diffractometer at 153 K (Al_{13}) and 173 K (Al_{13}·NH_4NO_3) K using MoK_α radiation (λ = 0.71073 Å). Absorption corrections were applied by SADABS. The structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least squares procedures on F^2. Highly disordered NO_3^- anions and solvent water molecules in the crystal structure of Al_{13} were treated by SQUEEZE.[22]

Correction of the X-ray data by SQUEEZE is 353 electrons/cell; the calculated value for these nine NO_3^- anions and seven water molecules in **Al_{13}** is 349 electron/cell. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms in **Al_{13}** were found on the difference F-map and refined with isotropic thermal parameters. Some of the H atoms in the coordinated water molecules in **Al_{13}** are disordered over three positions due to their involvement in three different H-bonds, and they were refined with occupation factor $\mu = 0.66$. H atoms in **Al_{13}·NH_4NO_3** were not found and have not been taken into consideration. There is also a partial occupancy NH_4^+ cation in **Al_{13}·NH_4NO_3** on a special position ($\mu = 0.5$). All calculations were performed by the Bruker SHELXTL package.

*Crystal data for $H_{90}Al_{13}N_{15}O_{102}$ (**Al_{13}**)*: $M_r = 2283.61$, colorless block, 0.31 × 0.18 × 0.09 mm, triclinic, space group *P*-1 (no. 2), $a = 12.8256(8)$, $b = 13.1667(8)$, $c = 13.4201(8)$ Å, $\alpha = 77.6010(10)$, $\beta = 74.0590(10)$, $\gamma = 87.6480(10)°$, $V = 2127.9(2)$ Å^3, $Z = 1$, $r_{calcd} = 1.785$ g·cm^{-3}, $\mu = 0.312$ mm^{-1}, $F(000) = 1180$, $2\theta_{max} = 56.58°$, 22455 reflections collected, 9682 unique [$R_{int} = 0.0203$], *R* indices [$I > 2\sigma(I)$]: $R1 = 0.0479$, w$R2 = 0.1267$, GOF = 1.069.

*Crystal data for $H_{96}Al_{13}N_{17}O_{106}$ (**Al_{13}·NH_4NO_3**)*: $M_r = 2381.68$, colorless block, 0.08 × 0.08 × 0.05 mm, triclinic, space group *P*-1 (no. 2), $a = 12.623(3)$, $b = 13.251(3)$, $c = 13.597(3)$ Å, $\alpha = 74.877(4)$, $\beta = 72.419(4)$, $\gamma = 86.790(4)°$, $V = 2092.4(2)$ Å^3, $Z = 1$, $r_{calcd} = 1.890$ g·cm^{-3}, $\mu = 0.326$ mm^{-1}, $F(000) = 1232$, $2\theta_{max} = 50.0°$, 15065 reflections collected, 7308 unique [$R_{int} = 0.0700$], *R* indices [$I > 2\sigma(I)$]: $R1 = 0.0836$, w$R2 = 0.1961$, GOF = 1.051.

Bridge to Chapter III

Two different homometallic tridecameric hydroxide clusters have now been synthesized, **Ga_{13}** and **Al_{13}**. The next step down the periodic table was to try and synthesize an In_{13} compound, but this compound has not been isolated to date. However, in the process of attempting to synthesize an In_{13} compound, binary mixtures of metal nitrate starting material salts were examined, which has led to the isolation of the heterometallic tridecameric hydroxide compounds that will be described in the following three chapters.

CHAPTER III

SYNTHESIS OF HETEROMETALLIC GROUP 13 NANOCLUSTERS AS INKS FOR OXIDE THIN-FILM TRANSISTORS

Introduction

I contributed to the work described in this chapter through the identification of the di-*n*-butylnitrosamine compound which allowed the isolation of these compounds in higher yields and larger quantities. Without this discovery, sufficient quantities of the Ga_7In_6 compound could not have been prepared. I also performed extensive rewriting of the paper after a direction shift, complete with final editing and addressing reviewer comments. Dr. Jason T. Gatlin originally synthesized the Ga_7In_6 cluster described in the chapter and wrote initial drafts of the paper prior to the direction shift. Dr. Stephen T. Meyers performed all TFT related studies (including X-ray powder diffraction) and wrote the relevant sections of the paper. Dr. Lev N. Zakharov performed all single-crystal X-ray diffraction studies and wrote the relevant X-ray data section of the paper. Prof. Douglas A. Keszler and Prof. Darren W. Johnson were the principle investigators for this work and provided editorial assistance. The results of this work were published in 2008 in *Angewandte Chemie, International Edition*, a publication of Wiley-VCH Verlag GmbH & Co. KGaA, volume 47 pages 9484-9486.[1]

We have recently reported high-yielding syntheses of two inorganic Group 13 metal-hydroxide nanoclusters: $[Ga_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (**Ga_{13}**, Figure 3.1, left) and $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (**Al_{13}**, Chapter II).[2,3] The $[M(\mu_3\text{-}OH)_6M_6(\mu\text{-}OH)_6]$ central fragment of these clusters forms a planar core with six additional $M(H_2O)_4$ groups bound to the core by two μ-OH bridges. The outer metal ions alternate above and below the plane formed by the central seven metal ions. Prior

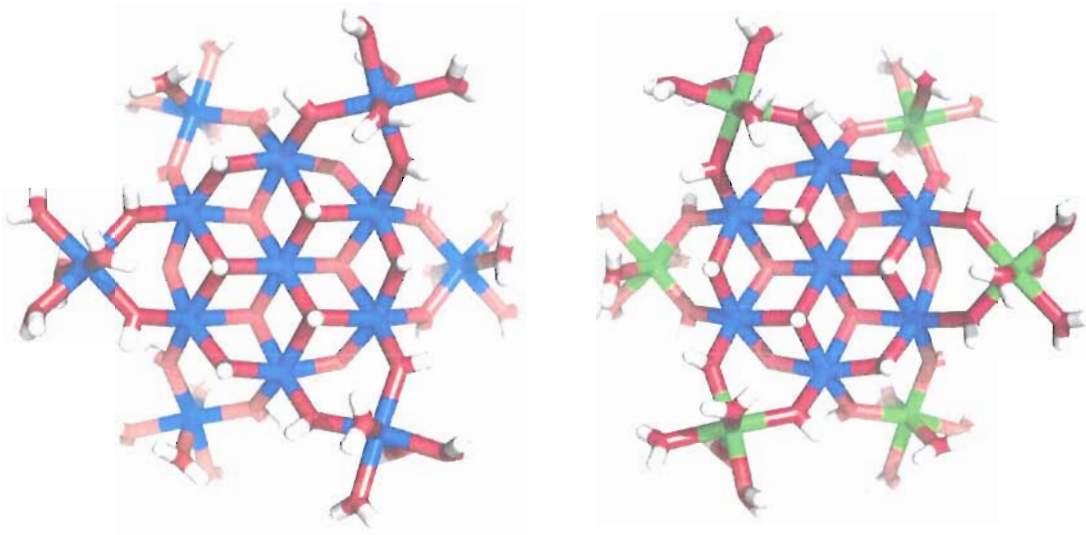


Figure 3.1. Structural representation of tridecameric Group 13 hydroxide clusters. On the left is a representation of the crystal structure of $[Ga_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (**Ga_{13}**) and on the right is a representation of $[Ga_7In_6(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (**Ga_7In_6**). Both are structurally similar, with **Ga_7In_6** having indium atoms (shown in green) in place of the outer ring gallium atoms of **Ga_{13}**. Images generated with PyMol.

synthetic preparation of Group 13 metal hydroxide compounds such as these has proven difficult. Their syntheses often require caustic or acidic conditions, elevated temperatures and pressures, and only provide clusters in low yields (sometimes only a

few single crystals). Crystallization periods of months or even years are not uncommon.[4-7] Owing to these difficulties, relatively few discrete Group 13 metal hydroxide clusters have been synthesized, though several striking examples of aluminum[4,5,7,8] and gallium[3,6,9,10] complexes have been reported. Both hydrated clusters and those stabilized by organic ligands are known, with a larger variety of ligand-supported clusters having been isolated, owing to enhanced stability resulting from lower charge density due to charge balance provided by the ligands.[4] In the case of these inorganic and ligand-supported compounds, neither heterometallic nor indium-containing clusters are known. However, in the case of Keggin-Al_{13} clusters, the central tetrahedral metal can be substituted, forming M_1Al_{12} structures (compounds with M=Al, Ga, or Ge are known, with others suggested).[11-14] To our knowledge though, no heterometallic Group 13 metal hydroxide clusters with multiple substitutions have been reported. Furthermore, the low-yielding, challenging syntheses often associated with these clusters have prevented attempts to explore applications requiring large quantities of such compounds. In order to address synthetic difficulties and to explore the use of these clusters as precursors for materials, I have developed an improved synthesis that affords heterometallic Group 13 nanoclusters of the type reported herein. Presented in this chapter is a new heterometallic gallium–indium cluster, $[Ga_7In_6(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}(NO_3)_{15}]$ (**Ga_7In_6**, Figure 3.1, right). This compound can be synthesized reliably, in yields ranging from 25 % to 95 %, by utilizing two different nitroso additives.[2,3] **Ga_{13}** and **Ga_7In_6** can both be prepared in gram-scale quantities which enables the unprecedented use of these nanoclusters as single-source solution precursors

for the deposition of oxide semiconductor thin films.[15,16] Such deposition provides a new route to the fabrication of high-performance thin-film transistors (TFTs) comprising spin-coated $In_{0.92}Ga_{1.08}O_3$ semiconductor layers.

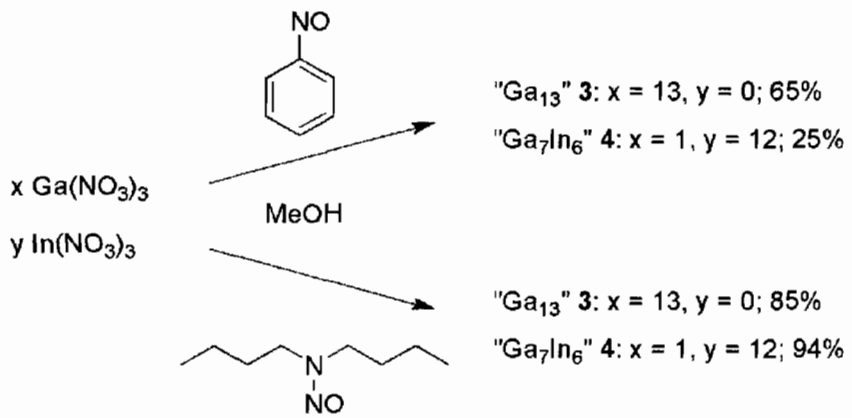
Materials Precursor Interest

There has been recent interest in the use of nanoscale cluster precursors to synthesize new materials.[17-20] The difficult syntheses of Group 13 metal hydroxide clusters have mostly prevented their use in these applications. Most solution precursors for printed oxide films involve controlled hydrolysis of metal-organic compounds and the condensation of metal-hydroxo sols that are then pyrolyzed to form the oxide. Such films are beset by a variety of density, defect, and segregation issues relating to the inhomogeneous nature of the sol, retention of significant organic components, or oxygen nonstoichiometry associated with organic burnout. From this perspective, soluble, all-inorganic, heterometallic hydroxide clusters, such as the M_{13} system, provide model precursors and an entirely inorganic, rapid, low-volume-loss condensation pathway, eliminating the aforementioned detrimental effects of organic moieties.

Synthetic Procedures for Tridecameric Clusters

Scheme 3.1 depicts synthetic routes to structures $\mathbf{Ga_{13}}$ and $\mathbf{Ga_7In_6}$ using two different nitroso compound additives. Applying the previously reported procedure of

adding nitrosobenzene to a 1:12 ratio of $Ga(NO_3)_3$ and $In(NO_3)_3$ affords single crystals of cluster **Ga_7In_6**, which are isolated in 25 % yield.[3] However, the manual separation of crystals from the tar-like product mixture limited the amount of material that could be isolated. To address the problems of difficult isolation and limited reaction scale, I sought alternatives to nitrosobenzene. The use of di-*n*-butylnitrosamine affords **Ga_{13}** and **Ga_7In_6** in superior yields of 85 % and 95 %, respectively.[2] The reaction with di-*n*-butylnitrosamine produces a mixture of a transparent oil (which can be reused in future



Scheme 3.1. Synthetic preparation of Ga_{13} and Ga_7In_6 by two different methods. The top route depicts the synthesis of **Ga_{13}** and **Ga_7In_6** using nitrosobenzene as the organic additive. The bottom method using di-*n*-butylnitrosamine affords the same compounds in much higher yields and larger scales. In both cases, a large excess of $In(NO_3)_3$ is required to form the fully substituted **Ga_7In_6** compound.

syntheses) and gram-scale quantities of single-crystalline **Ga_{13}** and **Ga_7In_6** products. Multiple characterization techniques confirmed that the bulk crystals isolated from the reaction and the single crystals reported herein are the same. This robust synthetic strategy enables the use of these clusters as precursors for bulk materials.

Optimized synthesis of $[Ga_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (**Ga_{13}**) *using an alternate organic additive.* Di-*n*-butylnitrosamine (1.15 g, 7.26 mmol, 24 equiv.) was added to gallium(III) nitrate hydrate (1.0 g, 3.91 mmol, 13 equiv.) in 10 mL of methanol, as a homogeneous solution. The mixture was evaporated over 10 days at which point the methanol and nitrosamine were no longer miscible and crystals began to form on the sides and bottom of the reaction vessel. After several more days the methanol completely evaporated giving a single yellow tinted liquid phase. The remaining oil was decanted and single crystals of **Ga_{13}** were washed with cold ethyl acetate (3 × 10 mL) and dried open to the atmosphere, providing the identical **Ga_{13}** cluster isolated by the previous nitrosobenzene route in 85 % yield with respect to $Ga(NO_3)_3$.

Preparation of $[Ga_7In_6(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (**Ga_7In_6**). Nitrosobenzene was utilized as the organic additive. Gallium(III) nitrate (1.73 mg, 0.006 mmol, 1 equiv.) and indium(III) nitrate (24.7 mg, 0.082 mmol, 12 equiv.) were dissolved in 5 mL of methanol. Nitrosobenzene (17.6 mg, 0.165 mmol, 24 equiv.) was dissolved in 2 mL of methanol, and the solutions were mixed together. The mixture was evaporated at room temperature over 10-12 days, yielding large single crystals of **Ga_7In_6** in 25 % yield with respect to gallium, although the crystals were embedded within the tar-like product mixture of decomposed nitrosobenzene (Figure 2.2).

Optimized preparation of $[Ga_7In_6(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (**Ga_7In_6**). This method uses di-*n*-butylnitrosamine instead of nitrosobenzene. Di-*n*-butylnitrosamine (0.93 g, 5.9 mmol, 24 equiv.) was added to a solution of $Ga(NO_3)_3$ (0.068 g, 0.267 mmol, 1 equiv.) and $In(NO_3)_3$ (0.872 g, 2.97 mmol, 12 equiv.) in 10 mL

methanol, and formed a homogenous solution. The mixture was evaporated at room temperature over 2 weeks, affording single crystals of **Ga_7In_6** in 94 % yield with respect to gallium (longer crystallization times generally increase the yield of the reaction). Di-*n*-butylnitrosamine was removed via syringe, and the remaining crystals were washed with cold ethyl acetate (3 × 10 mL) and dried in air.

Application as Precursor Inks for Thin-Film Transistors

To demonstrate the utility of the improved synthesis, we explored the use of these clusters in the fabrication of electronic devices, which is driven by a rising interest in printed macroelectronics and the high carrier mobilities recently reported in Group 13 and other *p*-block amorphous oxide semiconductors.[15,21,22] Our collaborators, the Keszler lab at Oregon State University, have recently described all-inorganic metal hydroxide cation condensation routes to dense, high-quality oxide dielectric films.[23,24] On the basis of these results, the discrete metal hydroxide clusters **Ga_{13}** and **Ga_7In_6** were immediately recognized as potential oxide precursors operating on similar principles. **Ga_7In_6** is of particular interest because of the large indium fraction and the excellent performance of In_2O_3-based semiconductors.[21,22]

Initial device characteristics of a TFT with an amorphous $In_{0.92}Ga_{1.08}O_3$ (IGO) semiconductor derived from a spin-coated aqueous solution of **Ga_7In_6** are presented in Figure 3.2; V_{on} = - 6 V and limited hysteresis is observed. On-to-off current ratios are

>106:1 for all devices fabricated on 100 nm thermally grown SiO_2 dielectric surfaces. Field-effect mobilities for these bottom-gate devices are approximately 9 $cm^2V^{-1}s^{-1}$ after annealing at 600 °C. Characterization of similar, thicker films by X-ray diffraction results in the pattern depicted in Figure 3.3. A single broad reflection centered near 2θ = 33° is consistent with previously reported amorphous IGO films.[15] A cross-sectional image of the same film recorded by scanning electron microscopy (Figure 3.3, top) shows a generally dense morphology with small inhomogeneities (<10 nm) possibly resulting from agglomeration of subcolloidal species during spin-coating.

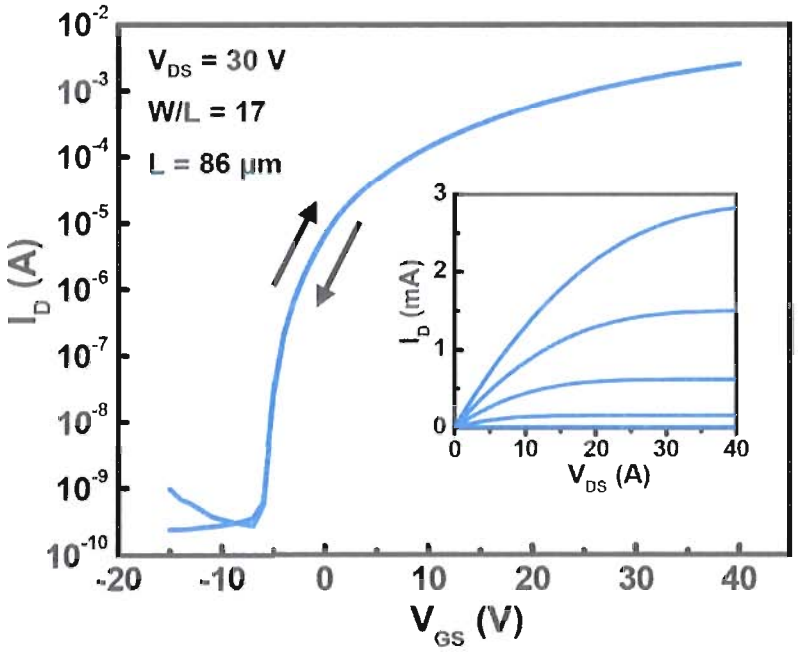


Figure 3.2. Representative transfer and (inset) output characteristics for a bottom-gate IGO-channel TFT with a 100 nm thermally grown SiO_2 dielectric surface. V_{GS} in the output curve is stepped from 0 – 40 V in 10 V steps. I_D = drain current; V_{DS} = drain-to-source voltage; V_{GS} = gate-source voltage; L = channel length; W = channel width.

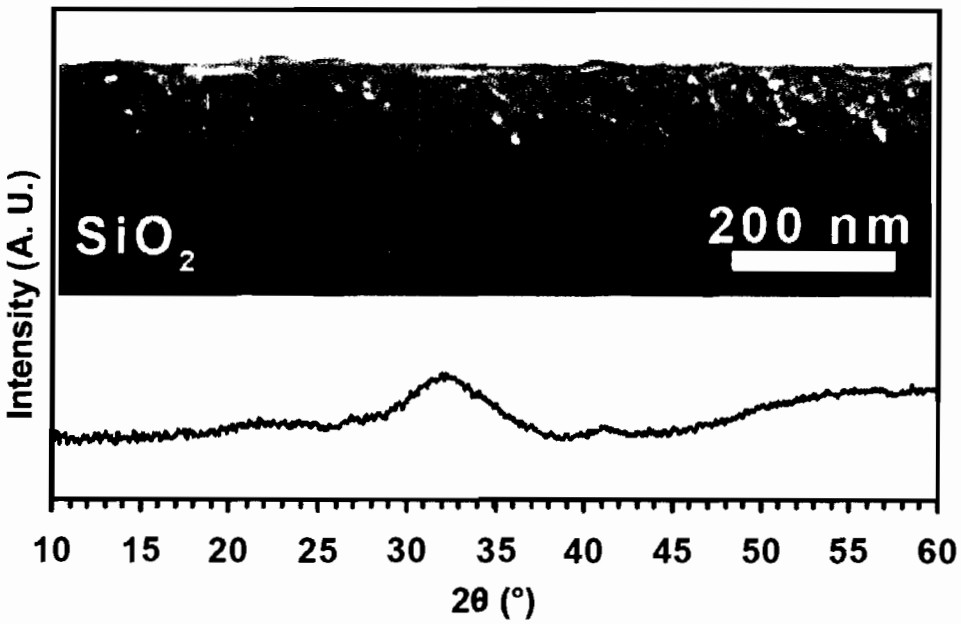


Figure 3.3. Thin-film XRD pattern (bottom) and cross-sectional SEM image of an $In_{0.92}Ga_{1.08}O_3$ film (top). The film was fabricated by spin-coating an aqueous solution of Ga_7In_6 followed by annealing at 600 °C for 1 hour in air. The broad peak seen in the XRD pattern indicates that the film is still amorphous in nature.

The direct deposition of such high-performance semiconductors from aqueous solutions is unprecedented and represents an important step toward printed macroelectronics. Thin-film X-ray diffraction was performed on a Rigaku RAPID diffractometer with Cu K_α radiation. TFTs were fabricated by dissolving Ga_7In_6 in deionized water with an initial resistance near 18 MΩ (Figure 3.4). This ink was deposited by spin-coating on *p*-type Si substrates capped with 100 nm of thermally grown SiO_2. Semiconductor/dielectric film stacks were then annealed for 1 h at 600 °C in air. Aluminum source and drain electrodes were evaporated through a shadowmask to

complete the device fabrication. TFTs were characterized in the dark using a Hewlett-Packard 4156C semiconductor parameter analyzer.

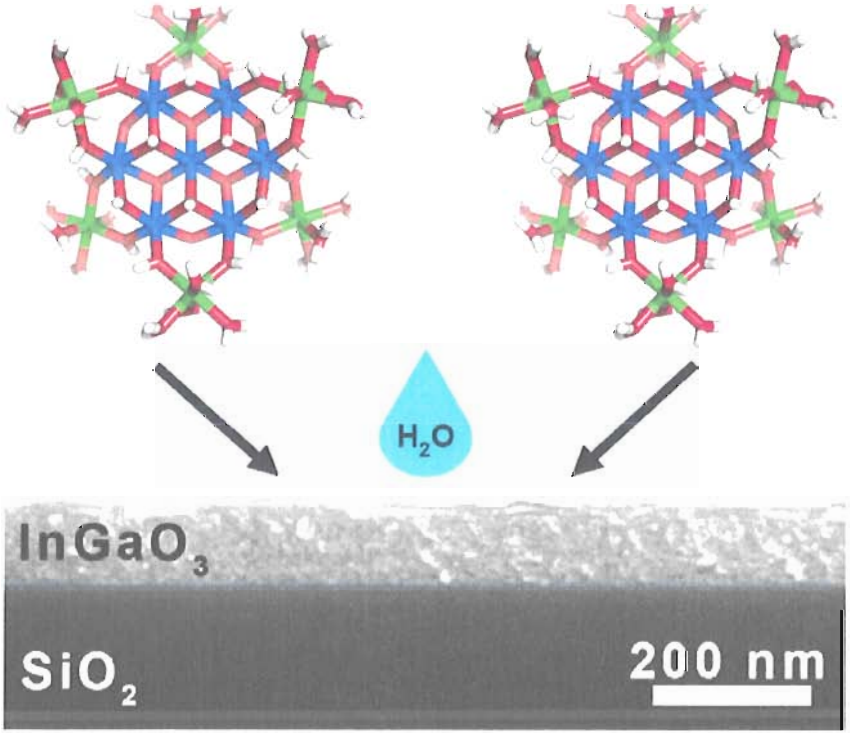


Figure 3.4. Representation of process to deposit IGO films from heterometallic precursors. Single-crystalline product isolated by the described method was dissolved in water and spin-coated onto SiO_2 substrates, followed by an annealing step at 600 °C for 1 hour. High quality, robust thin film metal oxides were generated with this method.

Conclusion

In summary, I have devised a synthetic strategy for making gallium clusters which utilizes a reusable reagent and proceeds relatively quickly, providing high yields of

the cluster at ambient temperature.[1] I expanded this strategy and showed general utility by synthesizing aluminum clusters and heterometallic gallium/indium congeners.[1,2] Insofar as these molecules might hold promise as single-source precursors for novel materials (as demonstrated by the IGO thin films reported herein), developing an efficient synthetic method is highly important. This work also perhaps sheds light on the mechanism of cluster growth. For example, previous work suggests that dimeric and octameric fragments might form initially.[6] This synthetic method led to no structures with varying compositions of the inner seven metal atoms, suggesting the M_7 core might be particularly stable. A recent report of an analogous ligand-stabilized Fe_7 cluster supports this hypothesis.[25]

Crystallographic Methods and Summary of Data

Experiments were carried out on a Bruker Smart Apex diffractometer at 153 K using MoK_α radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied by SADABS ($T_{min}/T_{max} = 0.767$). Crystals of **Ga_7In_6** are hexagonal, $R\,\bar{3}$ (no. 148). The **Ga_7In_6** cation is on a $\bar{3}$ axes, analogous to the related **Ga_{13}** cluster. **Ga_7In_6** is isostructural with **Ga_{13}**, possessing the same "$Ga(\mu_3\text{-}OH)_6Ga_6(\mu\text{-}OH)_6$" core, but with indium atoms in the exterior positions of the cluster connected via μ-OH bridges (Figure 3.1). The Ga-O distances range from 1.907 Å to 2.159 Å, while In-O distances range from 2.082 Å to 2.167 Å. Two NO_3^- anions (in general positions) provide twelve NO_3^- anions per **Ga_7In_6** cation. Three other NO_3^- anions and solvent methanol molecules (in

general positions as well) are highly disordered and randomly fill six other possible positions around the **Ga_7In_6** cation. Highly disordered NO_3^- anions and solvent methanol molecules were treated by SQUEEZE.[26] Corrections of the X-ray data by SQUEEZE (638 electrons/cell) are close to the required value of 603 electrons/cell for 9 NO_3^- anions and 18 methanol molecules in the full unit cell. All non-H atoms were refined with anisotropic thermal parameters. Hydrogen atoms have not been taken into consideration.

Refinements of the crystal structures of **Ga_7In_6** without symmetry restrictions on occupation factors for the gallium and indium atoms show that the refined occupation factors of the Ga(1), Ga(2), and In(1) atoms are very close to those based on the crystal symmetry. The Ga(1)-O and Ga(2)-O distances in this structure are comparable and close to the distances found in the related **Ga_{13}** cation. This indicates that in all of these structures the central M_7 cores of the M_{13} cations are composed of gallium atoms only. The average In-O(H_2O) distance in **Ga_7In_6**, 2.166(4) Å, is close to the distances found before in complexes with an In-O(H_2O) bond: for example, 2.156 and 1.158 Å were reported in catena-[(μ-oxalato-O,O',O'',O''')-bis(μ-O',O'',O''')-tetraaqua-diindium dihydrato].[27]

*$H_{72}Ga_7In_6N_{15}O_{93}$ (**Ga_7In_6**)·$6CH_3OH$*. M_r = 3139.94 , 0.21 × 0.18 × 0.12 mm, hexagonal, $R\bar{3}$ (no. 148), a = 20.6974(14) Å, b = 20.6974(14) Å, c = 18.256(3) Å, α = 90°, β = 90°, γ = 120°, V = 6773(1) Å^3, Z = 3, ρ_{calcd} = 2.310 g cm^{-3}, μ = 3.704 mm^{-1}, $F(000)$ = 4620, $2\theta_{max}$ = 54.00°, T = 153(2) K, 16375 reflections measured, 3290 reflections independent [R_{int} = 0.0187], $R1$ = 0.0246, $wR2$ = 0.0721 for 3290 reflections

(165 parameters) with $I > 2\sigma(I)$, and $R1 = 0.0256$, $wR2 = 0.0727$, and GOF = 1.102 for all 3290 data, max/min residual electron density +1.034/-0.406 e $Å^{-3}$.

Bridge to Chapter IV

We have now successfully demonstrated the utility of our synthetic procedure in making two homometallic M_{13} compounds (**Al_{13}** and **Ga_{13}**) as well as a heterometallic compound (**Ga_7In_6**) described in Chapter III. In Chapter IV, a full series of heterometallic Ga/In compounds with varying indium content will be described, as well as the first examples of Al/In heterometallic compounds. Additional characterization details are also provided for these compounds.

CHAPTER IV

PREPARATION OF A SERIES OF NOVEL HETEROMETALLIC TRIDECAMERIC GROUP 13 HYDROXIDE CLUSTERS

Introduction

I contributed to this work through the isolation of several of the new Ga/In clusters, as well as the Al_8In_5 cluster. I also did the primary writing of the manuscript that is to be submitted for publication. Sharon A. Betterton performed the variable-temperature powder X-ray diffraction experiments and analyzed the resultant data. Maisha K. Kamunde-Devonish isolated the Al_9In_4 structure. Dr. Jason T. Gatlin isolated Ga/In clusters, performed the electron probe microanalysis characterization, and sent samples for elemental analysis. Dr. Lev N. Zakharov is responsible for all single-crystal X-ray data. Prof. Darren W. Johnson and Prof. Douglas A. Keszler were the principle investigators for this work and provided editorial assistance.

The Group 13 metals, particularly gallium and aluminum, possess a "bewildering variety of behavior" and often exhibit similar hydrolytic behavior.[1] In solution, the Group 13 metals exist in a dynamic series of species from water-ligated monomers to hydroxide oligomers, dependent upon pH and concentration variables.[2-10] In contrast to this, surprisingly few discrete Group 13 metal hydroxide structures have been isolated and characterized. It is likely that their "bewildering variety of behavior" is what has hindered the successful isolation of discrete structures, making isolation of one major product difficult. Aluminum has received much attention due to its environmental prevalence and effects such as its implication in the transport of heavy metals downstream from mining areas, in addition to observed phytotoxicity of some aluminum oligomers themselves.[2,5,7,8,11-14] Gallium and indium clusters have also been studied, albeit to a lesser extent.[4,6,9,15] I have described hydroxide structures containing each of these metals in the preceding chapters; **Ga_{13}**, **Al_{13}**, and a heterometallic **Ga_7In_6**.[8-10,15] We sometimes refer to these structures as "flat" to differentiate them from the more widely studied Keggin-Al_{13} structures.[7,16,17] However, this chapter will continue to use abbreviated nomenclature referring to the metal content of the clusters only; i.e. $[Ga_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ or "flat-Ga_{13}" will be designated as **Ga_{13}** (Figure 4.1).[15]

Until our original report of the **Ga_{13}** structure, the only Group 13 metal hydroxide structures that had been isolated as purely inorganic structures were aluminum-based (Al_2, Al_8, and Al_{13} hydroxides were known), with the lack of structures likely owing testament to the difficulty of their synthesis and isolation.[2,5,6,18] Such compounds are usually isolated through hydrolysis of metals salts, in combination with heating or other

steps. Fedin and co-workers also reported the isolation of $\mathbf{Ga_{13}}$ utilizing curcurbit[6]uril and pyridine in the crystallization process, though the exact role of cucurbit[6]uril is unknown.[6] The judicious choice of supporting ligands bound to the exterior metal sites in place of water molecules has enabled the synthesis of a wider variety of Group 13 hydroxide structures.[3,4,12,19,20] Aminocarboxylate ligands such as *N*-(2-hydroxyethyl)iminodiacetic acid (H_3heidi) have been used to synthesize ligand-supported versions of $\mathbf{Al_{13}}$ and $\mathbf{Ga_{13}}$, as well as several lower nuclearity structures.[4,21,22] It is suggested that bound ligands act to balance charge and control hydrolysis activity.[12,20] A summary of relevant clusters (both inorganic and ligand-supported) is found in Chapter I.

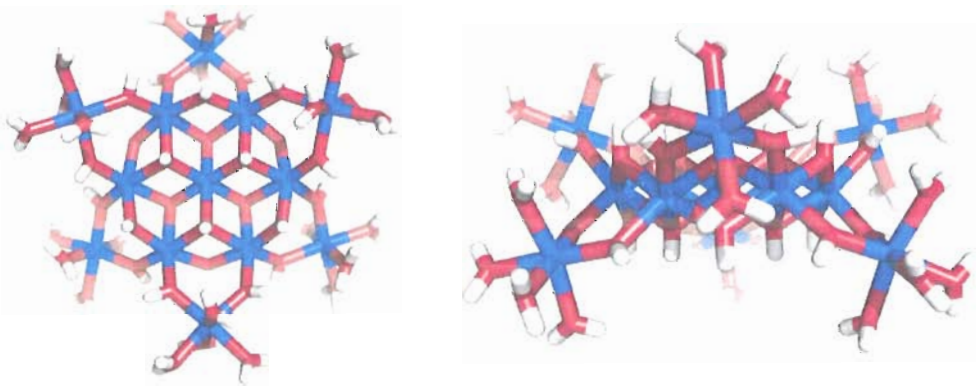


Figure 4.1. Top and side view of a tridecameric cluster. On the left can be a top view of tridecameric structure. The profile view showing the up-and-down alternation of the outer ring of metal centers is seen on the right. Metal ions are blue, oxygen red, and hydrogen white. Image generated with PyMol.

One problem with many of these preparations (for both the inorganic and ligand-supported clusters) has been the lack of wide utility. Many procedures result in the

isolation of only one or two structures, making a more general synthetic strategy highly desirable. Another common pitfall is the limited scale and low isolated yields for many of these metal hydroxides. The syntheses often provide only a few crystals of the reported compounds.[2] Such issues have largely hindered the application of these clusters in areas such as materials precursors. Perhaps more notably, in both the purely inorganic and the ligand-supported structures, one cluster type has been absent: a heterometallic hydroxide structure with a mixture of Group 13 metal ions.

I described in Chapter III the first example I have encountered of this heterometallic hydroxide structure type, and also described the use of this compound as a single-source precursor for the fabrication of solution processed amorphous metal oxide thin films.[9] This expanded on our previous isolations of $\mathbf{Ga_{13}}$ and $\mathbf{Al_{13}}$ and began to show a broader applicability of this synthetic method. Three distinct metal coordination environments are seen in these tridecameric metal hydroxide clusters (Figure 4.1). The metal ions are bridged to each other by hydroxide groups, with water ligands filling the four remaining coordination sites of the exterior metal ion sites. The central metal ion is bound to six μ_3-OH ligands while the six interior ring metals are bound to two μ_3-OH and four μ-OH ligands each. The six exterior metal ions are coordinated to two μ-OH ligands and four water molecules. More comprehensive descriptions of the metal center coordination environments are given in the "Structural Description" sections of this chapter.

Our synthesis of these clusters proceeds through an unusual course, whereby Group 13 metal nitrate salts are dissolved in methanol with an organic nitroso compound

as an additive. These solutions are then evaporated open to air at room temperature; within two weeks crystals begin to form on the bottom of the scintillation vials. With the $\mathbf{Ga_{13}}$ and $\mathbf{Ga_7In_6}$ clusters, yields up to 85 % and 95 %, respectively, were achieved using the di-*n*-butylnitrosamine additive.[9] Using a slightly altered procedure with added base (NaOH, NH_4OH, or $Al(OH)_3$), I was able to form the $\mathbf{Al_{13}}$ cluster as well, albeit in lower yields and with the formation of other inorganic salts.[8] To isolate the $\mathbf{Ga_7In_6}$ cluster, a large excess of indium nitrate salt is required to drive formation of the fully indium-substituted cluster: a one-to-twelve ratio of gallium nitrate to indium nitrate was used. The natural curiosity was whether varying equivalents of indium could be incorporated into the heterometallic clusters as well. In follow-up to the previous chapters, Chapter IV describes a full series of heterometallic $Ga_{7+x}In_{6-x}$ (x = 1 - 5) hydroxide structures which are isolated in similar yields to the previously discussed $\mathbf{Ga_7In_6}$ heterometallic cluster, in addition to the first heterometallic Al/In hydroxide clusters: $\mathbf{Al_8In_5}$ and $\mathbf{Al_9In_4}$.

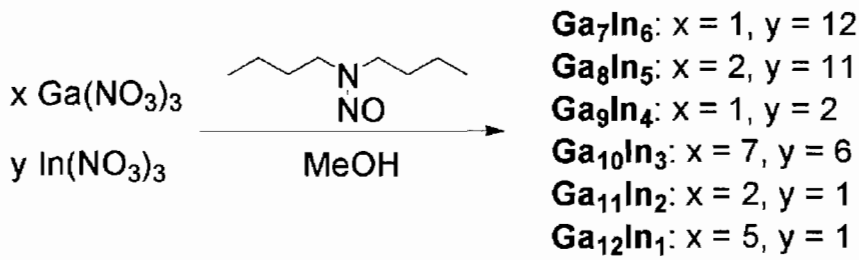
Experimental Details

General Methods. All reagents were purchased from commercial sources and used as received. Gallium and indium nitrate salts were purchased from Strem Chemicals. Aluminum nitrate was obtained from our reuse facility and originally manufactured by Baker and Adamson. Di-*n*-butylnitrosamine was purchased from TCI America. Methanol was also used as received, with no drying attempted. Unless

specified, all reactions were conducted in standard 20 mL scintillation vials, open to atmosphere and at room temperature.

Synthesis of Ga/In Heterometallic Compounds

Synthesis of $[Ga_{7+x}In_{6-x}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (***Ga_7In_6, Ga_8In_5, Ga_9In_4, $Ga_{10}In_3$, $Ga_{11}In_2$, $Ga_{12}In$***). Methanolic solutions of $Ga(NO_3)_3$ and $In(NO_3)_3$ were prepared. Di-*n*-butylnitrosamine was added to these solutions via a syringe. The solutions were shaken vigorously, uncapped, and evaporated at room temperature. After several weeks, clear, colorless, cubic single crystals of the heterometallic Ga/In clusters formed on the bottom of the vials in > 90 % yield, as calculated with $Ga(NO_3)_3$ as the limiting reagent and assuming six H_2O ligands per $Ga(NO_3)_3$ equivalent. Crystals were isolated by decanting the remaining pale yellow liquid or removing it with a syringe, then rinsing the product crystals with ethyl acetate. Alternately, an acetone wash also effectively washes away residual nitroso compound. The synthetic details are the same for all of the heterometallic Ga/In clusters, with the only difference being the starting $Ga(NO_3)_3$:$In(NO_3)_3$ ratios which are as follows: **Ga_7In_6** requires a 1:12 ratio, **Ga_8In_5** requires a 2:11 ratio, **Ga_9In_4** requires a 1:2 ratio, **$Ga_{10}In_3$** requires a 7:6 ratio, **$Ga_{11}In_2$** requires a 2:1 ratio, and **$Ga_{12}In$** requires a 5:1 ratio (Scheme 4.1).



Scheme 4.1. Starting material ratios for Ga/In clusters. The number of $Ga(NO_3)_3$ equivalents are presented as the x values, while the $In(NO_3)_3$ equivalents are presented as the y values.

Synthesis of Heterometallic Al/In Compounds

*Synthesis of $[Al_9In_4(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (**Al_9In_4**).* A solution of $Al(NO_3)_3$ (0.251 g, 8 equiv.) and $In(NO_3)_3$ (0.126 g, 5 equiv.) was prepared in 3.2 mL of a 0.26 M NaOH solution in MeOH. Di-*n*-butylnitrosamine (0.318 g, 24 equiv.) was then added to the solution via a syringe. The solution was shaken vigorously until all solids were dissolved, uncapped, and the solvent evaporated over several weeks. If a large amount of solid has precipitated, the mixture can be filtered. A mixture of crystalline material is obtained, with larger crystals on the sides of the vial that are potentially $M(NO_3)_3$ salts, sodium salts, $Al(OH)_3$, $In(OH)_3$, or other inorganic impurities. On the bottom of the vial, smaller crystals form which contain the desired product. As with the Ga/In clusters, the remaining liquid was decanted or removed with a syringe, then crystals were rinsed with ethyl acetate to remove the residual di-*n*-butylnitrosamine. The same cluster has been isolated using an 9:4 ratio of $Al(NO_3)_3$ to $In(NO_3)_3$ as well.

Synthesis of $[Al_8In_5(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (***Al_8In_5***). The same synthetic procedure used to isolate **Al_9In_4** was used for **Al_8In_5** except either 6:7 or 7:6 ratios of $Al(NO_3)_3$ to $In(NO_3)_3$ were applied in the synthetic procedure.

Description of Characterization Methods

Single-crystal X-ray Diffraction (*XRD*). XRD experiments were carried out on a Bruker Smart Apex diffractometer at 153 K and 173 K using Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were applied by *SADABS*. The structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures on F^2. Highly disordered NO_3^- anions and solvent methanol molecules were treated by SQUEEZE.[23] In the case of **Ga_7In_6**, corrections of the X-ray data by SQUEEZE (638 electrons/cell) are close to the required value of 603 electrons/cell for 9 NO_3^- anions and 18 methanol molecules in the full unit cell. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms have not been taken into consideration. Refinements of the crystal structure of **Ga_7In_6** without symmetry restrictions on occupation factors for the gallium and indium atoms show that the refined occupation factors of the Ga(1), Ga(2), and In(1) atoms are very close to those based on the crystal symmetry. The data from the other heterometallic structures were analyzed by the same method.

Electron probe microanalysis. Electron probe microanalysis (EPMA) measurements were carried out on a Cameca SX100 and analyzed with Probe for EPMA

software. The measurements were normalized to the number of oxygen atoms, and the number of gallium and indium atoms calculated relative to this.

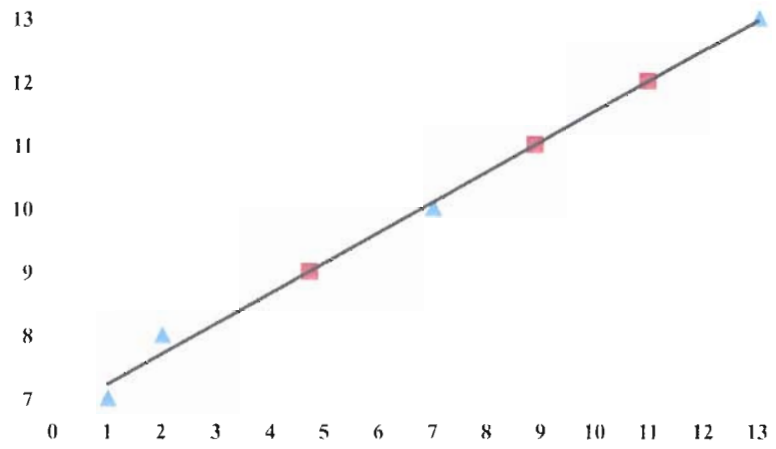
Elemental Analysis. Elemental analysis (EA) on compounds was conducted by Desert Analytics. Samples of bulk amounts of single-crystalline material were sent and used for analysis.

Powder X-ray Diffraction. Powder X-ray diffraction data were collected on a Rigaku Miniflex diffractometer with Cu Kα radiation.

Description of Synthesized Compounds

Based on the successful isolation of the $\mathbf{Ga_{13}}$ and $\mathbf{Al_{13}}$ structures, we also examined binary metal nitrate mixtures, first those containing gallium and indium. The first heterometallic cluster we chose to target was one with full indium substitution in the six peripheral metal positions, $[Ga_7In_6(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$, ($\mathbf{Ga_7In_6}$). A 7:6 ratio of $Ga(NO_3)_3$ to $In(NO_3)_3$ was used in the reaction. Analysis of the single-crystalline product showed the actual gallium-to-indium ratio to be 10:3 ($\mathbf{Ga_{10}In_3}$). Based on this observation, it was suspected that an excess of $In(NO_3)_3$ would be required to achieve substitution of all six gallium centers. To verify this, a 1:12 $Ga(NO_3)_3$-to-$In(NO_3)_3$ ratio was used, which successfully afforded the $\mathbf{Ga_7In_6}$ cluster. Following this, a 2:11 ratio of $Ga(NO_3)_3$ to $In(NO_3)_3$ was tested and afforded a $\mathbf{Ga_8In_5}$ cluster. Graphing these three Ga/In heterometallic compounds along with $\mathbf{Ga_{13}}$ using the number of gallium atoms in the product cluster as the y-axis values and number of starting gallium

equivalents (out of 13 total metal equivalents) as the x-axis values provided a linear fit (Graph 4.1). This fit was used to predict the starting material ratio for the missing Ga/In structures. Calculating missing y values of 9, 11, and 12 (the number of gallium atoms in the desired product cluster for the $\mathbf{Ga_9In_4}$, $\mathbf{Ga_{11}In_2}$, and $\mathbf{Ga_{12}In}$ compounds, respectively), we were able to predict the required starting material ratios to be roughly 1:2 (4.71:8.29), 2:1 (8.88:4.12), and 5:1 (10.97:2.03) of $Ga(NO_3)_3$ to $In(NO_3)_3$ for $\mathbf{Ga_9In_4}$, $\mathbf{Ga_{11}In_2}$, and $\mathbf{Ga_{12}In}$, respectively (Graph 4.1). Applying these ratios, we successfully synthesized the remaining clusters, as confirmed by single-crystal X-ray diffraction experiments. Bulk characterization techniques have confirmed the metal ratios in these clusters. Both EDS and EA were performed on the isolated bulk solids, and showed only slight variation from the compositions determined by single-crystal XRD in the case of the $\mathbf{Ga_{10}In_3}$ and $\mathbf{Ga_7In_6}$ compounds (Table 4.1).



Graph 4.1. Graph used for Ga/In ratio prediction of missing clusters. X axis values represent the number of $Ga(NO_3)_3$ equivalents used (out of 13 total). Y axis values are gallium equivalents in the product cluster. The blue triangles represent the known clusters; red squares represent the predicted values.

Table 4.1. Characterization data for cluster compounds. The table summarizes data gathered by single-crystal XRD, EA, and EPMA. The data for the bulk characterization methods (EA and EPMA) matches the data collected by single-crystal XRD, except in the case of $\mathbf{Ga_{10}In_3}$, where EA gave a ratio closer to $\mathbf{Ga_9In_4}$, and $\mathbf{Ga_7In_6}$, where both EA and EPMA determine a ratio closer to $\mathbf{Ga_6In_7}$. Data collected by Dr. Jason Gatlin.

	Starting Material		*Characterization*					
			XRD		EA		EPMA	
	Gallium	*Indium*	*Gallium*	*Indium*	*Gallium*	*Indium*	*Gallium*	*Indium*
$\mathbf{Ga_{13}}$	13	0	13	0	13	0	-	-
$\mathbf{Ga_{12}In}$	5	1	12	1	12	1	12	1
$\mathbf{Ga_{11}In_2}$	2	1	11	2	11	2	11	2
$\mathbf{Ga_{10}In_3}$	7	6	10	3	9	4	10	3
$\mathbf{Ga_9In_4}$	1	2	9	4	-	-	-	-
$\mathbf{Ga_8In_5}$	2	11	8	5	-	-	-	-
$\mathbf{Ga_7In_6}$	1	12	7	6	6	7	6	7

I have observed one other case of such a high degree of control over metal content in heterometallic clusters. Cronin and co-workers were able to demonstrate metal ratio control in dodecanuclear Ni/Co clusters using both starting material stoichiometry and solution pH.[24] Utilizing a carbonate core template, *cis,trans*-1,3,5-triaminocyclohexane, and acetate directing ligands, they were able to isolate both the homometallic Ni_{12} and Co_{12} complexes, as well as a series of heterometallic clusters. In our system, starting material stoichiometry is exclusively used to control the metal ratio. While the similar size and electron count of Co and Ni prevented differentiation of the metals in their system, the relative position of gallium and indium atoms are determined in our clusters, however the exact location of the indium atoms and their arrangement within the outer ring metal position cannot be determined, as an average of the six positions is seen crystallographically. This is discussed in more detail in the following section.

Structural Description of Ga/In Compounds

Characterization of the heterometallic Ga/In metal hydroxide clusters by single-crystal X-ray diffraction shows a structure similar to that observed in the previously reported **Ga_{13}**, **Al_{13}**, and **Ga_7In_6** clusters. As an example, crystals of **Ga_7In_6** are hexagonal, $R\bar{3}$ (no. 148). The **Ga_7In_6** cation is on a $\bar{3}$ axes, analogous to the related **Ga_{13}** cluster. Two NO_3^- anions (in general positions) provide twelve NO_3^- anions per **Ga_7In_6** cation. Three other NO_3^- anions and solvent methanol molecules (in general positions as well) are highly disordered and randomly fill six other possible positions around the **Ga_7In_6** cation. In addition to characterization by full data collections, we are able to roughly characterize the different compounds by unit cell volumes—the unit cell volume increases as more indium atoms are incorporated, from ~6494 $Å^3$ for **Ga_{13}** to 6774 $Å^3$ for **Ga_7In_6**.

Three different metal positions can be assigned in these compounds; **M1**, **M2**, and **M3** (Figure 4.2). All compounds feature a conserved planar core of seven gallium atoms (**M1** and **M2**) bridged by μ_3- and μ-OH ligands. **M1** is the central metal atom, bridged via μ_3 hydroxyl ligands to a ring of six more metal atoms (**M2**). **M2** metal centers are bound to each other through six μ-OH bridges. Six more metal atoms (**M3**) are bound to the **M2** centers through twelve μ-OH bridges. In the case of **Ga_7In_6**, the six bond distances between **M1** and the μ_3 oxygen atoms average to 1.966 Å. The average bond length between the μ_3 oxygen atoms and the six **M2** metal centers is 2.113 Å. Six μ-OHs bridge the six **M2** gallium atoms, with an average bond distance of 1.915 Å. The six **M3** metal atoms are bound to the core by μ-OH bridges and alternate above and below the

plane of the central atoms. The average **M3**–μ-OH distance is 2.086 Å. It is in this outer ring of metal ions only that indium atoms are found, ranging from one indium to six. Each outer ring metal atom (either Ga(III) or In(III)) fills its coordination sphere with four water ligands. The average In–O(H_2O)bond length is 2.166 Å. This is close to the distances found before in complexes with an In-O(H_2O) bond: for example, 2.156 and 2.158 Å were reported in catena-[(μ-oxalato-O,O',O',O''')-bis(μ-O',O'',O''')-tetraaqua-diindium dihydrato].[25]

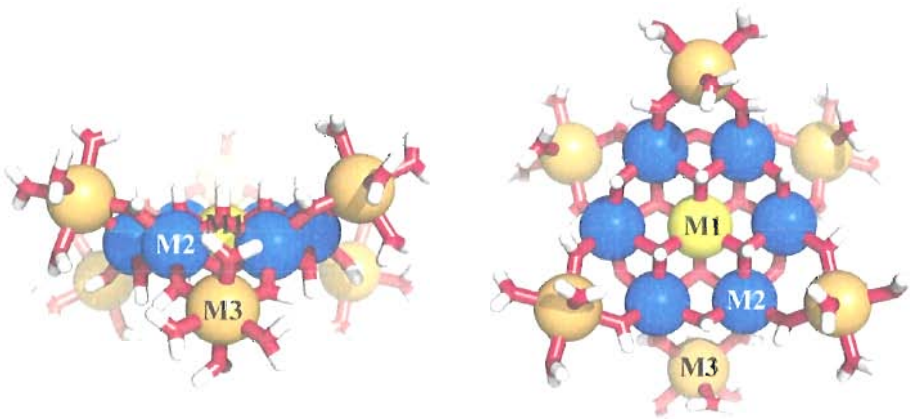


Figure 4.2. Three different metal centers are found in the clusters. **M1** is the central metal site, **M2** are the ring of six metal sites that form the remainder of the planar core, and **M3** metal centers occupy the exterior metal sites and alternate above and below the central planar core.

These clusters crystallize in $R\bar{3}$ with **M1** on the $\bar{3}$ special position, so only one **M2** and **M3** from each of the next six-metal rings is unique. Because of this, the electron count for the outer metal position is an averaged number representative of the gallium-to-indium ratio. Solving for this ratio determines the number of indium atoms. In some

cases, partial atom values are obtained for gallium and indium stoichiometries, such as $Ga_{10.3}In_{2.7}$. Such a ratio could result from a crystal structure containing a mixture of **$Ga_{10}In_3$** and **$Ga_{11}In_2$** clusters, with a $Ga_{10.3}In_{2.7}$ stoichiometry representing a 70:30 ratio of the clusters in the solid state, though a more broad product distribution is possible, even likely. We have not ruled out the possibility that other metal stoichiometries exist within the same crystal, and crystals characterized as **$Ga_{10}In_3$** contain molecules with **Ga_9In_4**, **$Ga_{10}In_3$**, and **$Ga_{11}In_2$** stoichiometries, if not even more.

Because only one **M3** site is observed and the averaged electron count is used for quantification, we cannot determine the precise location of indium atoms in relation to each other. For example, there are three potential arrangements for **M3** indium atoms in **$Ga_{10}In_3$**: all indium atoms next to each other, two next to each other with the third separated by a gallium atom, or all three alternating with gallium atoms (analogous to the 1,2,3; 1,2,4; or 1,3,5 substitution patterns in benzene, Figure 4.3). I have postulated that the arrangement with alternating gallium and indium atoms is most likely, as it affords the most space between the larger indium atoms and would be the most symmetric of the species. However, a mixture of the possible "isomers" is likely present and any claims of regioselectivity represent conjecture at this stage.

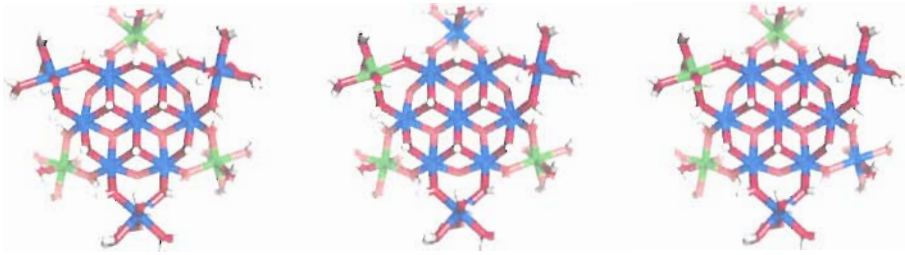


Figure 4.3. Different potential arrangements of the outer ring gallium and indium metal centers. Three different arrangements are possible for the six outer ring metal centers. A staggered pattern is depicted on the left; an arrangement with two neighboring indium centers is in the middle, and on the right is an arrangement with all indium and gallium atoms neighboring each other. Gallium atoms are blue; indium atoms are green. Images generated with PyMol.

Structural Description of Al/In Compounds

Single-crystal X-ray diffraction was used to characterize these compounds and their structures were, as expected, very similar to the other tridecameric Group 13 metal hydroxides described in this dissertation. Unlike the $\mathbf{Al_{13}}$ structure which is triclinic, these aluminum containing structures are rhombohedral, as are $\mathbf{Ga_{13}}$ and all the Ga/In heterometallic structures. Similar to the synthesis of $\mathbf{Al_{13}}$ however, the addition of base is required in order to produce these clusters. We propose the same rationale as that case—the Lewis acidity of aluminum is less than that of gallium or indium, and therefore to promote the formation of hydroxide bridges, base must be added to aid the deprotonation of water ligands.[8,26] In both Al/In compounds, there are again three different metal environments, though the **M3** position contains both aluminum and indium. Using Al_8In_5 as a example, the Al–O bond distance from **M1** to μ_3-OH is 1.897 Å. The average μ_3-OH

to **M2** distance is 2.075 Å. The average bond length from **M2** aluminum atoms to the μ-OH ligands bridging the **M2** sites is 1.859 Å. The average distance between **M3** and the μ-OH ligands that bridge **M3** to the core is 2.083 Å. Lastly, the average In–O(H_2O) distance is 2.156 Å. Figure 4.4 pictorially summarizes all the cluster compounds that have been synthesized to date.

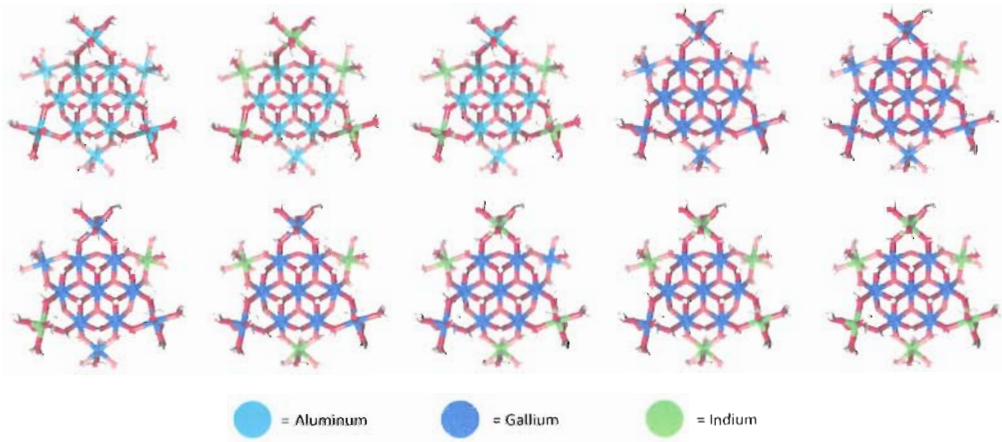


Figure 4.4. Summary of tridecameric clusters. To date ten different compounds have been isolated and characterized. Three aluminum-based compounds have been isolated (**Al_{13}**, **Al_9In_4**, and **Al_8In_5**) and seven gallium-based compounds (**Ga_{13}**, **$Ga_{12}In$**, **$Ga_{11}In_2$**, **$Ga_{10}In_3$**, **Ga_9In_4**, **Ga_8In_5**, and **Ga_7In_6**). In the case where multiple regioisomers are possible, the highest symmetry isomer is shown. Images generated with PyMol.

Variable-temperature Powder X-ray Diffraction

To understand the effect varying Ga:In ratios have on the decomposition properties of $Ga_{7+x}In_{6-x}$ clusters, bulk samples were calcined and studied via XRD. As illustrated in Figure 4.5, dehydration of crystalline **Ga_{13}** produces a white amorphous

solid that persists to ~600 °C. By 700 °C, reflections indicative of monoclinic gallium oxide (β-Ga_2O_3) are evident. The decomposition behavior of **$Ga_{10}In_3$** is similar (Figure 4.6), demonstrating a loss of crystallinity upon dehydration. Here, the material (also white) remains amorphous up to ~800 °C. At 900 °C, peaks attributable to β-Ga_2O_3 are clearly evident, and intensities increase with heating. Of note in these patterns is the shift of Ga_2O_3 peaks to lower 2θ values with increasing indium content, indicating an increase in cell volume. Similar behavior is observed during the heating of **Ga_9In_4** (Figure 4.7). The white powder remains amorphous to ~800 °C, and at ~900 °C, β-Ga_2O_3 peaks emerge, again shifted to lower 2θ values from the reference peaks.

The results of calcining the indium-rich **Ga_8In_5** (Figure 4.8) and **Ga_7In_6** (Figure 4.9) are distinct from those of the previous compounds. There is no amorphous phase formed upon heating either sample to 200 °C; rather, peaks consistent with the cubic In_2O_3 structure type are present, and the powders are yellow. This phase is stable to ~800 °C, and at ~900 °C, β-Ga_2O_3 peaks become apparent. The material remains a mixture of both phases to 1100 °C.

The incorporation of indium into the β-Ga_2O_3 structure has been previously studied, and it is known that indium preferentially substitutes O_h Ga sites, forming a β-$GaInO_3$ structure.[27,28] These studies have demonstrated that the substitution of the larger indium results in an increase in the a, b, and c lattice parameters and a decrease in the β parameter, changes that ostensibly produce a shift of β-Ga_2O_3 peaks to lower 2θ values, which we observed in our studies.[28] These peak shifts, as a function of indium content, are detailed in Figure 4.10. As In_2O_3 peaks emerge in the oxides formed from **Ga_8In_5**

and $\mathbf{Ga_7In_6}$, and we observe no significant peak shifts above x = 0.62, our system appears to have a saturation limit between x = 0.62 (32 mol %) and x = 0.77 (38 mol %). This value is smaller than that reported by Edwards et al. (42 mol %),[27] but falls within the range reported by Shannon and Prewitt (33-50 mol %).[28]

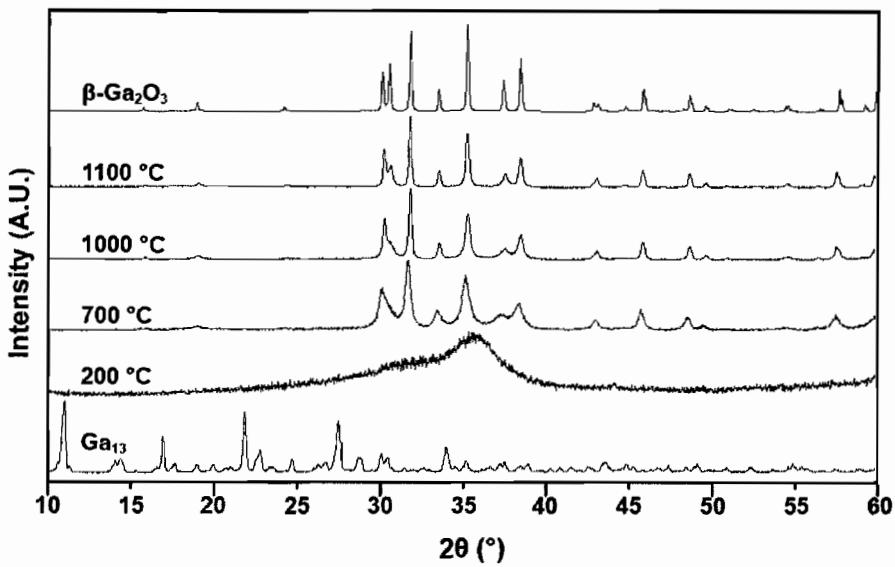


Figure 4.5. X-ray diffraction traces for Ga_{13}. Variable-temperature powder X-ray diffraction patterns for bulk powder of $\mathbf{Ga_{13}}$.

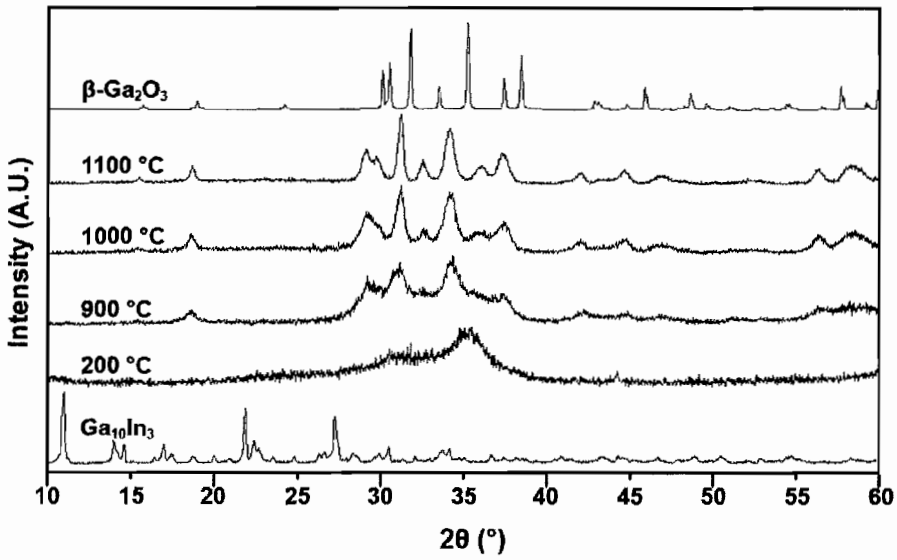


Figure 4.6. X-ray diffraction traces for $Ga_{10}In_3$. Variable-temperature powder X-ray diffraction patterns for bulk powders of **$Ga_{10}In_3$**.

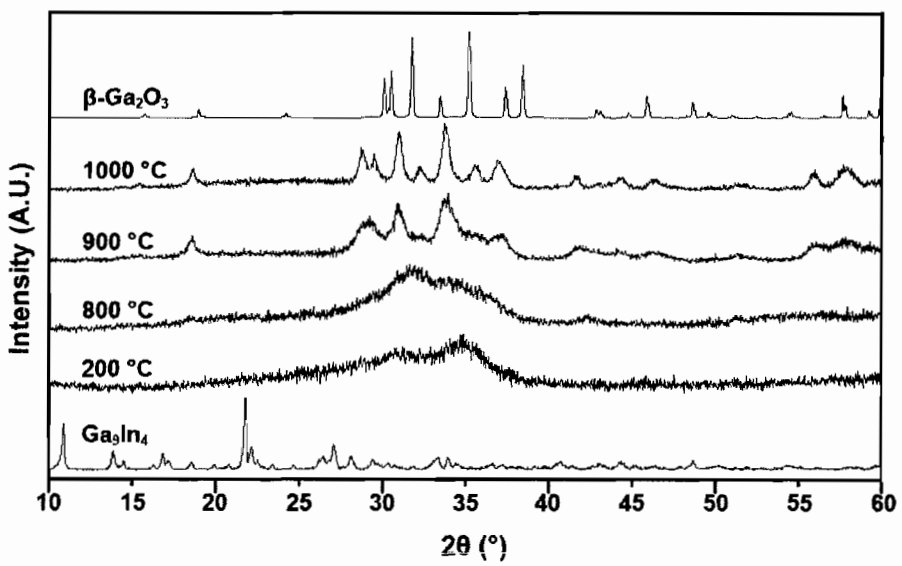


Figure 4.7. X-ray diffraction traces for Ga_9In_4. Variable-temperature powder X-ray diffraction patterns for bulk powders of **Ga_9In_4**.

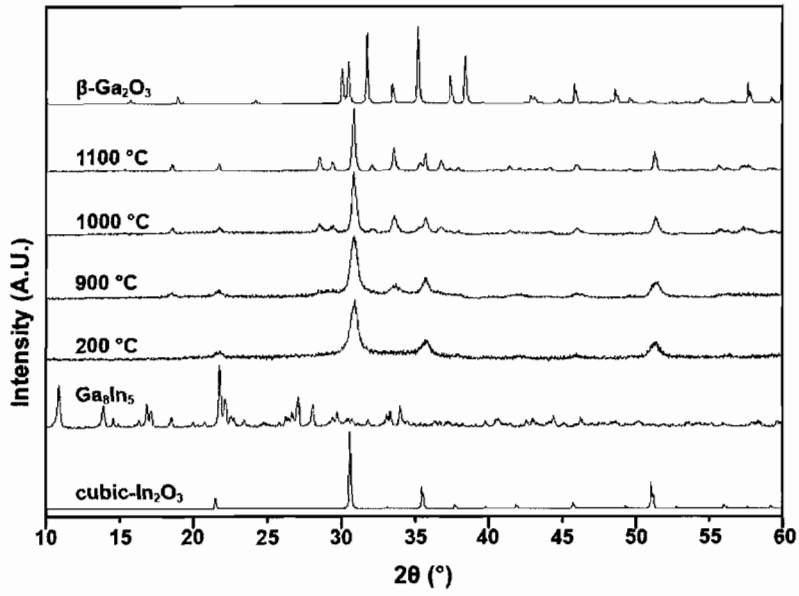


Figure 4.8. X-ray diffraction traces for Ga_8In_5. Variable-temperature powder X-ray diffraction patterns for bulk powders of **Ga_8In_5**.

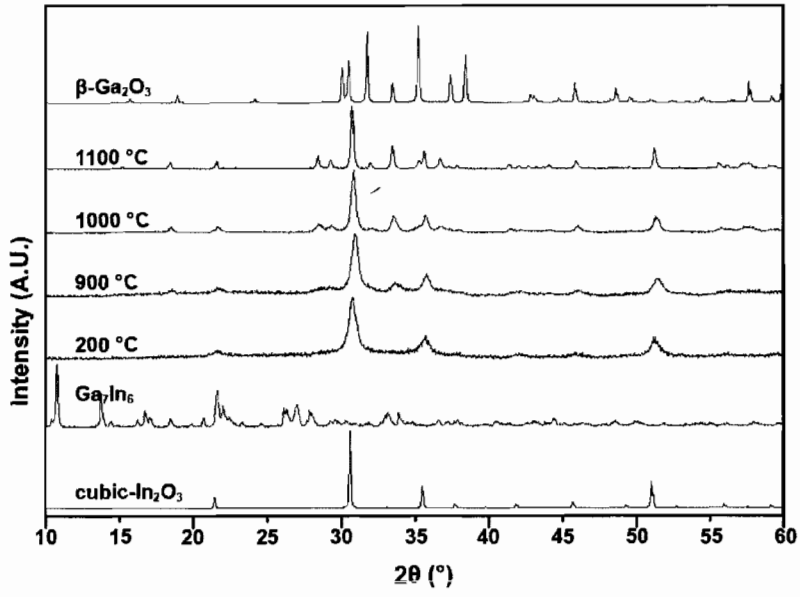


Figure 4.9. X-ray diffraction traces for Ga_7In_6. Variable-temperature powder X-ray diffraction patterns for bulk powders of **Ga_7In_6**.

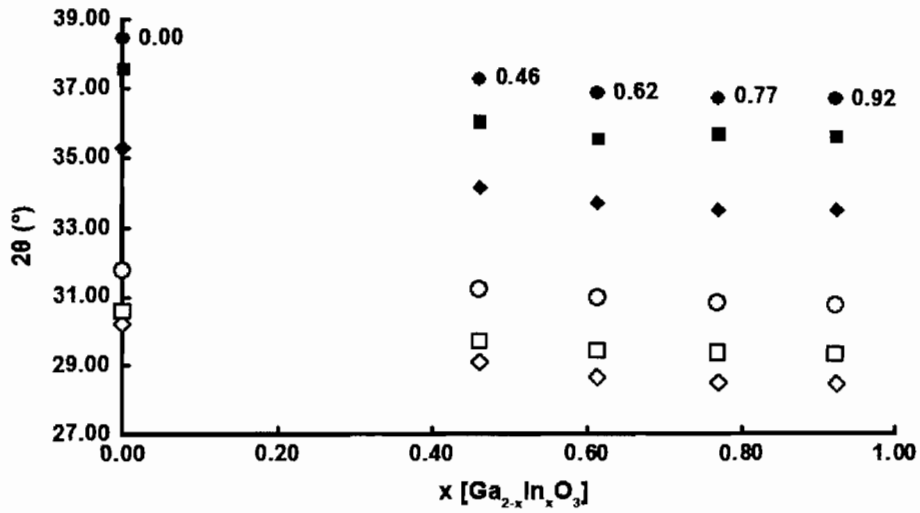


Figure 4.10. 2θ values of five strong β-Ga_2O_3 peaks. The 2θ values decrease as a function of mole fraction In (x): (◊) 30.06 °, (□) 30.50 °, (○) 31.74 °, (♦) 35.18°, (■) 37.38 °, (●) 38.40 °.

Discussion of Cluster Formation

One common question in this synthetic procedure concerns the role of the nitroso compounds. The Ga_{13} cluster has been isolated in the presence of three different nitroso-containing organic molecules, as well as in the presence of cucurbit[6]uril.[6,9,15] In the case of nitrosobenzene, it was found that nitrosobenzene was oxidized to nitrobenzene during the reaction (as shown by NMR and mass spectrometry) which was thought to consume nitrate counterions from the solution and thereby facilitate condensation of the gallium atoms based on availability of counterions. In the case of di-*n*-butylnitrosamine, which is now used almost exclusively for these reactions, I observed no evidence of oxidation to the corresponding nitroamine, either by NMR or mass spectrometry, after the

course of several months open to air (Figure 4.11). At the same time we achieve higher yields and larger reaction scales with this nitroso compound than with either of the previous ones (nitrosobenzene and a proprietary ligand), which naturally led to questions regarding the role of the nitroso functionality in this series of reactions. To add further uncertainty, both $\mathbf{Ga_{13}}$ and $\mathbf{Ga_9In_4}$ have been isolated in the absence of nitroso

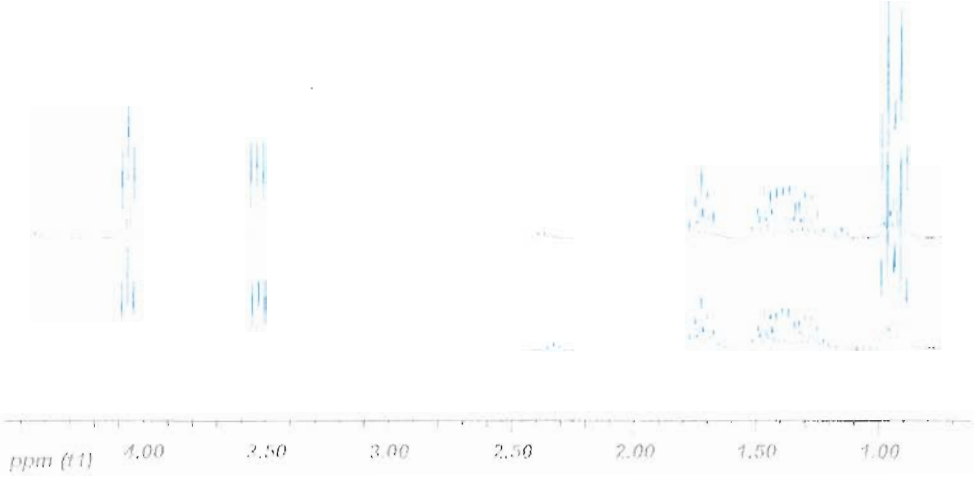


Figure 4.11. NMR spectra of di-*n*-butylnitrosamine. The top spectrum of di-n-butylnitrosamine was taken before a $\mathbf{Ga_{13}}$ synthesis reaction. The bottom spectrum was taken after a $\mathbf{Ga_{13}}$ synthesis, from di-n-butylnitrosamine recovered from the scintillation vial.

compounds, by simply dissolving $Ga(NO_3)_3$ or a mixture of $Ga(NO_3)_3$ and $In(NO_3)_3$ in MeOH and evaporating the solution. In these cases, the crystallization generally takes much longer and the syntheses are less reliable, however yields have been shown to be comparable, with yields of 80+ % having been achieved. Additionally, when a methanolic $Ga(NO_3)_3$ solution is placed in a vapor diffusion chamber with ethyl acetate, similar to the method used to produce the Ga- and In-acetate chains I will describe in

Chapter VI, **Ga_{13}** was again isolated.[10] Crystals formed on the bottom of the vial were confirmed as **Ga_{13}**, with a yield of 83 %. Aside from our own work, Fedin and coworkers have also been able to isolate Ga_{13} in the absence of a nitroso compound, using cucurbit[6]uril and pyridine instead.[6] The role of the cucurbit[6]uril is also unclear however, and the authors were unable to isolate the **Ga_{13}** compound in its absence through variations in Ga(III) concentrations, temperature, and pH.

With multiple examples of isolation in the absence of a nitroso compound, what is the role played by the nitroso compound in the reaction? One postulate is that the nitroso compounds are slightly basic, as the oxygen of the nitroso functionality can be protonated. This slight increase in basicity may aid in the formation of the hydroxide bridges needed to produce the clusters. Another suggestion involves solubility: $Ga(NO_3)_3$ and **Ga_{13}** are not soluble in di-*n*-butylnitrosamine, but are readily methanol soluble. The methanol evaporates much more quickly than nitrosamine, creating a system similar to vapor diffusion. The solubility properties of the solution steadily change to those of the nitrosamine, encouraging the crystallization of **Ga_{13}**. The slow evaporation that results leads to reliable isolation of the clusters.

It has recently been suggested by Prof. Bill Casey that using methanol as the solvent is key as well, by slowing down the hydrolysis activity and controlling aggregation by limiting the amount of H_2O available to form the hydroxide bridges.[29] This agrees with our findings that the clusters can form in absence of a nitroso compound, but the nitroso functionality clearly plays a role, speeding up crystallization and making for a more reliable, easily isolated product. We believe the use of MeOH as

solvent is a key element to this synthesis, compared to most syntheses of Group 13 hydroxide structures where water is the solvent. As stated, this is believed to slow down the hydrolysis of the Ga(III) ions, and better facilitate aggregation and crystallization of the tridecameric cluster over more random products.

Conclusion

In conclusion, we have been able to demonstrate control over the metal ratios in a series of heterometallic Ga/In and Al/In tridecameric metal hydroxide clusters. These represent the first such heterometallic clusters of their kind, and have implications for the use of such clusters as single-source precursors for the fabrication of indium-gallium oxide and gallium oxide thin film semiconductors. Single-crystalline product is generated with tuned gallium-to-indium ratios in high-yielding, gram-scale syntheses. Such a wide range of potential materials would enable highly specific control of the material content of thin films made from these precursor compounds. Variable-temperature powder X-ray diffraction studies reported in this chapter suggest interesting decomposition behavior of the different potential precursor materials, particularly because we may have a possible route to prepare indium-gallium oxide thin films versus films with separated indium oxide/gallium oxide areas based on the gallium-to-indium ratio in the clusters used. We also hope that the preparation of these clusters will enable the isolation of additional heterometallic clusters. We are currently looking into the incorporation of metals other than those in Group 13, which if achieved may also hold

potential for the fabrication of additional thin film metal oxides. With the knowledge that heterometallic clusters are achievable, other researchers may wish to reexamine previous syntheses for the possibility of adding additional heterometallic structures to the examples presented in this chapter.

Bridge to Chapter V

I have described the synthetic preparation and uses of a series of homometallic and heterometallic tridecameric hydroxide clusters in Chapters II, III, and IV. In an effort to further derivatize these compounds and expand their applications, we next sought ways to achieve post-synthetic modification of the tridecameric structures.

CHAPTER V

POST-SYNTHETIC MODIFICATION AND POTENTIAL CHEMICAL APPLICATIONS OF CLUSTER COMPOUNDS

Introduction

I contributed to the work herein by developing and performing the procedures and composing the communication detailing the results. Matthew M. Baseman contributed to the results through the determination of yields for the metal exchange reactions and exploration of other possible isolable clusters. Laura A. Thompson also contributed to the findings through additional exploration of potential metal exchange reactions. Dr. Lev N. Zakharov performed all crystallographic studies. Prof. Darren W. Johnson was the principal investigator for this work and provided editorial assistance.

Throughout this dissertation I have described a series of homo- and heterometallic tridecameric Group 13 metal hydroxide clusters.[1-4] The first of these isolated was $[Ga_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (**Ga_{13}**).[4] Group 13 metal hydroxide clusters such as **Ga_{13}** represent an area of broad scientific interest. In addition to their importance to basic scientific research, they have many practical applications and real-world implications. Many aluminum hydroxide species have either been proven or proposed to exist in natural aqueous solutions.[5-7] Some such species are used to flocculate and remove heavy metal ions from solution, while others have been shown to transport heavy metals out of mining areas contributing to heavy metal pollution. Additionally, some of the compounds are directly phytotoxic.[7,8] The traditional syntheses of these clusters can often be problematic, with extensive reaction/crystallization times and low isolated yields. We have previously demonstrated an improved synthetic procedure for making the **Ga_{13}** and $Ga_{7+x}In_{6-x}$ compounds that has proven to be high-yielding and scalable (Chapter III).[3] Using this, we have shown that **Ga_{13}** and $[Ga_7In_6(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (**Ga_7In_6**) hydroxide clusters can be used as single-source solution precursors for thin film metal oxide semiconductors.[3]

Following the successful isolation of a series of tridecameric Group 13 hydroxide clusters (as described in Chapters II, III, and IV) and demonstration of some of their applications (i.e. thin film precursors, Chapter III) I sought to further expand their usefulness.[1-3] Post-synthetic modification represents a potential method, giving several options to control the properties of the cluster compounds. Using structures prepared by our developed synthetic route, I proposed structural modification through two potential

routes: introduction of new metals by metal exchange reactions or functionalization of the clusters through ligand exchange reactions. There is prior literature precedent in related cluster compounds for both metal exchange and ligand substitution.[9,10] In both situations, solution stability of the cluster compounds is a paramount concern in achieving the desired transformation. In metal exchange reactions, the outer metal centers must be labile enough to be replaced by competing metal ions. In the case of ligand exchange, the clusters must persist in solution and not fully disassociate, which would leave no exterior metal ions to bind to ligands.

There are three potential degrees of solution stability. The clusters may be fully stable in solution, they may partially dissociate, or they may fully dissociate. We can dissolve the clusters in, and recrystallize them from, protic solvents (H_2O and MeOH) as well as successfully implement them as single-source precursors for metal oxide thin films, which gives evidence for some degree of solution stability/aggregation.[3] In order to test the solution stability of our clusters, we sought to find out how and to what extent our clusters participate in metal and/or ligand exchange reactions by investigating three pertinent research questions: 1) Are the six peripheral metal centers labile in solution, 2) Do homogeneous conditions facilitate exchange of water ligands by organic ligands, and 3) Would heterogeneous or biphasic reaction conditions facilitate ligand exchange?

Summary of Experimental Approach

First off, I chose to investigate whether the six outer ring metal ions in **Ga_{13}** are labile in solution. If **Ga_{13}** clusters partially or fully dissociate in solution, the presence of an excess of $In(NO_3)_3$ might promote the formation of heterometallic clusters upon solvent evaporation, as in our previously established synthesis of **Ga_7In_6**. No evidence for an In_{13} cluster has been observed, so any indium incorporation should be due to dissociation and replacement of outer ring gallium ions. These studies were performed with and without DBNA additive and over different time periods.

The second question concerned organic ligand exchange with the H_2O ligands of **Ga_{13}** in solution. Protons on the clusters (from bridging hydroxide and H_2O ligands) rapidly exchange in protic solvents, and as a result lack an appropriate handle for ^1H NMR characterization. Substitution of water ligands for ligands with non-exchangeable protons could provide such a handle for NMR characterization. Free ligands should exhibit chemical shifts different from those of ligands bound to clusters, which in turn may also exhibit different chemical shifts from ligands bound to monomeric gallium. In experiments investigating this issue, **Ga_{13}** was dissolved in either H_2O or MeOH and combined with various ligands, sometimes with pyridine to help deprotonate and solubilize the ligand. Examples of suitable ligand classes examined include benzene carboxylates, bipyridines, and catechols. My research in this area examined the extent of solution stability and feasibility of ligand exchange and characterization.

The last research question described in this chapter concerns whether or not organic-soluble ligands can be bound to **Ga_{13}** under heterogeneous or biphasic reaction

conditions. Organic-soluble ligands were dissolved in *p*-xylene and other high-boiling organic solvents containing a suspension of solid **Ga_{13}**. The solutions were then heated above 100 °C to drive off coordinating water ligands, promoting the exchange of ligands. X-ray crystallography and NMR were then used to analyze the success and degree of ligand exchange.[11] Biphasic layering experiments were also conducted, in which ligands were dissolved in organic solvents and the **Ga_{13}** clusters in H_2O or MeOH.

To address the questions outlined above, experimentation was undertaken to examine the overarching question of solution stability. All experiments utilized single crystalline **Ga_{13}**, chosen because of synthetic ease, structural simplicity (only gallium atoms), and apparent solution stability. Some of the first studies looking at the solution stability of **Ga_{13}** were performed using ^{69}Ga NMR. Samples were prepared as aqueous solutions of $Ga(NO_3)_3$ and **Ga_{13}** and spectra were recorded on a 500 MHz NMR spectrometer. The chemical shift of aqueous $Ga(NO_3)_3$ was recorded, set to 0 ppm (a value characteristic of octahedral gallium), and used as a reference peak. In solution, the **Ga_{13}** cluster showed a similar peak centered around 0 ppm, perhaps slightly broader in nature. As a result, it is unlikely that **Ga_{13}** is forming tetrahedral species in solution, as tetrahedral species would exhibit a different chemical shift. However, these results were inconclusive in terms of showing whether **Ga_{13}** was stable in solution. Rather, they showed that gallium was present in octahedral coordination only and gallium NMR was ruled out as an effective technique to evaluate solution speciation.

Metal Exchange Background

Our foray into this field was initially quite serendipitous, discovering an interesting synthesis of the tridecameric hydroxide compounds featuring the addition of organic molecules with nitroso functional groups to methanolic solutions of metal nitrate salts. Expanding on this, the synthesis of a series of heterometallic Ga/In tridecameric clusters was achieved. These compounds have indium atoms replacing gallium atoms in the outer ring of metal atoms. Indium composition can range from one to six atoms in these positions, as detailed in Chapters III and IV. The heterometallic clusters are synthesized from a mixture of $Ga(NO_3)_3$ and $In(NO_3)_3$ starting materials. I streamlined this technique using di-*n*-butylnitrosamine to give 80+ % yields of the **Ga_{13}** compound and 90+ % yields of the heterometallic Ga/In clusters.[3] One significant drawback to this synthesis is the large excess of $In(NO_3)_3$ required to isolate clusters with greater indium substitution. For example, **Ga_7In_6** requires a 1:12 ratio of $Ga(NO_3)_3$ to $In(NO_3)_3$. We suspect this may be due to the solubility of $In(NO_3)_3$ in di-*n*-butylnitrosamine; it is soluble while $Ga(NO_3)_3$ and the tridecameric clusters are both insoluble. I examined ways to address this excess requirement, in addition to examining the solution stability of these clusters. I discovered that the same heterometallic clusters can be produced starting with **Ga_{13}** by performing a metal exchange reaction with $In(NO_3)_3$ to yield $[Ga_{7+x}In_{6-x}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$, which requires significantly less $In(NO_3)_3$ than our previously reported procedure.

Metal exchange reactions have been reported in Keggin and Anderson clusters (Figure 5.1), which are similar to our tridecameric M_{13} compounds. In Keggin-Al_{13}, the

Figure 5.1. Representation of Keggin-Al_{13}, Anderson, and M_{13} clusters. In both the Keggin and Anderson clusters, the central metal can be exchanged; in our M_{13} clusters, the six peripheral metal atoms can be exchanged.

central tetrahedral metal atom can be replaced by Ga or Ge.[12] In Anderson clusters, a variety of di- and trivalent metal atoms have been substituted in the central position of the $Mo_7O_{24}^{6-}$ clusters.[13,14] Based on these well-established phenomena in these related cluster types, I explored the possibility for metal exchange in our clusters. In this section, the results of metal exchange studies are presented wherein methanolic solutions of **Ga_{13}** and $In(NO_3)_3$ are generated, which upon crystallization produce heterometallic $Ga_{7+x}In_{6-x}$ clusters. These clusters are structurally identical to those previously isolated. The metal exchange—where octahedral, non-central metal atoms are substituted—represents the first example I have observed of such behavior in Group 13 metal hydroxides. In the case of Keggin-Al_{13} metal exchange, only the single central metal which is bound by oxide ligands is replaced, whereas up to five metal atoms in the exterior position are exchangeable using the method described in this chapter.[8,15] This method reduces the excess of indium equivalents that are required to form the heterometallic clusters with

higher indium atom substitution, which in turn reduces the amount of di-*n*-butylnitrosamine required, as this amount is proportional to that of the metal nitrate.[3]

Metal Exchange Procedure

My decision to make Ga/In heterometallic structures by the addition of $In(NO_3)_3$ to a solution containing **Ga_{13}** was chosen because neither In_{13}, nor any other oligomeric indium hydroxide cluster has been observed. As a result, it was assumed that the presence of indium in the final structure would occur through incorporation of indium atoms into the **Ga_{13}** structure by a metal exchange process. **Ga_{13}** (0.10 g, 0.037 mmol), $In(NO_3)_3 \cdot nH_2O$ (0.27 g, 0.897 mmol), and di-*n*-butylnitrosamine (0.20 g, 1.27 mmol) were dissolved in 10 mL of methanol. After the solution was evaporated, crystals formed which were determined to be $[Ga_8In_5(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ by single-crystal X-ray diffraction. Such metal exchange can also be achieved in water or MeOH; **Ga_{13}** and $In(NO_3)_3 \cdot nH_2O$ are dissolved in 10 mL of H_2O or MeOH with no nitrosamine present. These reactions give the same products as those isolated with the nitrosamine present. The use of H_2O lengthens evaporation times, but both procedures (MeOH or H_2O only) eliminate the use of additional di-*n*-butylnitrosamine, a desirable outcome due to the expense and hazards associated with this compound. The reverse reaction can also be achieved. If **Ga_7In_6** is dissolved in MeOH with $Ga(NO_3)_3 \cdot nH_2O$, gallium centers can be introduced into the structures upon recrystallization. While interesting, this result is

less synthetically useful than the procedure to synthesize the indium-inclusive structures from **Ga_{13}** (Figure 5.2).

I also examined the effect of time on structural composition and it appears that the metal exchange results are independent of solution "aging" time. In the initial study, identical solutions were prepared with one opened and evaporated immediately after dissolving the $In(NO_3)_3 \cdot nH_2O$ and **Ga_{13}** crystals. The other vial was left capped on a shelf for one and a half months, after which time the solution was heated slightly for one hour and then evaporated. Both reactions produced the same **Ga_8In_5** structure, though the product crystals in the longer reaction have a slightly smaller unit cell volume, generally indicative of a smaller indium composition, though some variation is also expected due to differences in the H_2O:MeOH ratio of interstitial solvent molecules.

This procedure reduces the excess of indium atoms required to form the heterometallic clusters. In the case of the **Ga_8In_5** structure, a 2:11 ratio of $Ga(NO_3)_3$:$In(NO_3)_3$ was required to produce the cluster using the original procedure.

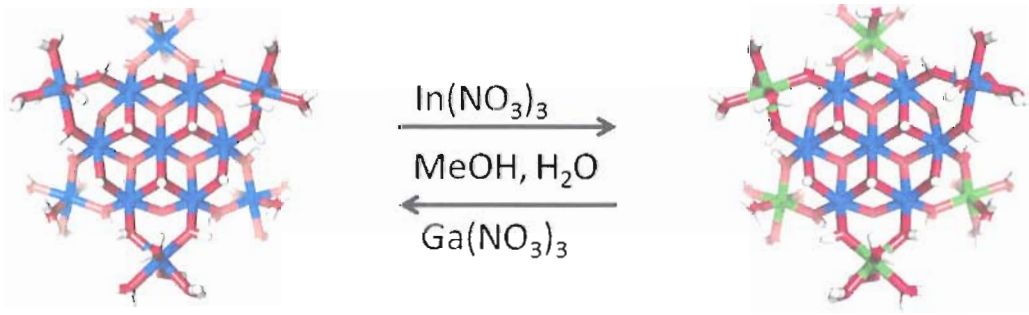


Figure 5.2. Depiction of metal exchange process. Tridecameric hydroxide clusters are dissolved in MeOH or H_2O with an excess of $In(NO_3)_3 \cdot nH_2O$ or $Ga(NO_3)_3 \cdot nH_2O$. The metal salt ions replace the exterior shell metal ions upon crystallization (as determined by single-crystal X-ray diffraction).

To produce the same cluster by the metal exchange reaction, a 1:24 ratio of **Ga_{13}** to $In(NO_3)_3 \cdot nH_2O$ is used, which translates to roughly a 1:2 ratio of Ga:In when considering each equivalent of the gallium cluster contains thirteen gallium atoms. Indium is not particularly abundant and its nitrate salts are expensive, so cutting back on the number of equivalents used in each reaction is highly desirable for enabling applications of this cluster.

This result also affords clues regarding the solution stability of these clusters. While we remain uncertain of the full extent of solution stability, it does suggest that clusters are partially, but perhaps not entirely, stable in solution. It was previously suspected that the inner core of seven metals was particularly stable. In this situation, the metal core is again conserved with no indium substitution in the inner core. It is likely that the inner core of seven metal atoms is stable and the outer six gallium atoms are somewhat labile in solution. We collected EXAFS data seeking to explore the extent of this solution stability as well, and preliminary results suggest a degree of solution stability based on the similarity of the collected spectra of dissolved **Ga_{13}** to a fit based on data from the single-crystal structure of **Ga_{13}** (Figure 5.3).

Potential Route to New Cluster Compositions

In additional to providing a less indium intensive method for producing the Ga/In heterometallic structures, the described metal exchange procedure for these tridecameric clusters may open the door for other metal exchange reactions as well. Such

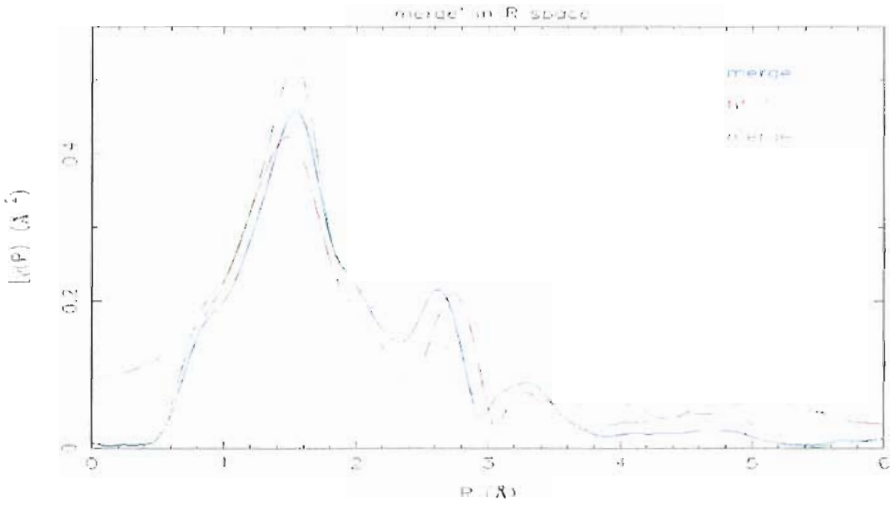


Figure 5.3. Preliminary EXAFS data. This figure (generated with the Artemis software package) depicts three different sets of EXAFS data in R space. The blue trace (*merge*) represents aqueous $\mathbf{Ga_{13}}$. The red trace (*fit 1*) is a fit generated from single-crystal X-ray diffraction data of solid phase $\mathbf{Ga_{13}}$. The green trace (*merge*) is aqueous data for $Ga(NO_3)_3$.

possibilities include many metals that have not successfully been incorporated into M_{13} clusters, offering a chance to isolate new heterometallic structures. To this end, other metal nitrate salts have been examined for incorporation into the M_{13} framework. Experiments to investigate this possibility were set up similarly to the indium exchange reaction. Metal nitrate salts (or salts with other counteranions as availability necessitated) were dissolved in solutions of $\mathbf{Ga_{13}}$, followed by evaporation of solvent. Initially, metals most similar to indium in hydrolysis constant (pK_a) were examined, as they should be hydrolyzed under similar conditions to In(III) ions. Such metals include Hg^{2+}, Al^{3+}, Sc^{3+}, Cr^{3+}, and Th^{4+}. These metal centers encompass a variety of ionic radii, so it might be possible to discern the importance of that factor in isolation of the

heterometallic clusters, as we feel this also explains the inability to isolate In_{13}. Additional metal ions such as Ru^{3+} and Fe^{3+} were tested based on our interest in the potential heterometallic structures. In initial studies, anywhere from six to thirty equivalents (versus $\mathbf{Ga_{13}}$) of metal salts were dissolved in MeOH solutions with $\mathbf{Ga_{13}}$ and di-*n*-butylnitrosamine. With Ru^{3+}, both the chloride and nitrosyl nitrate salts were tested. Both afforded viscous brown/red liquids. In the case of $Fe(NO_3)_3$/$\mathbf{Ga_{13}}$ solutions, the effect of pH on reactions was tested through added HCl and NaOH. In all cases, the only crystalline product isolated was recrystallized $\mathbf{Ga_{13}}$, although in some cases no crystalline material was isolated at all. Looking to the future, the addition of base may be necessary with metals of higher pK_a values in order to initiate formation of the hydroxide bridges necessary for synthesis and crystallization of the clusters. We remain optimistic that this method will provide access to a host of new heterometallic structures. DFT studies could also prove useful in evaluting the relative stabilities of heterometallic structures in order to determine which metal ions might prove fruitful.

Ligand Exchange Background

Another method I examined to modify the metal hydroxide clusters is through ligand exchange reactions. In the tridecameric clusters, each of the outer six metal ions is coordinated to four H_2O ligands. In solution, these H_2O ligands are expected to be in rapid exchange with solvent molecules (either H_2O or MeOH), giving the opportunity to replace them. Ample precedent for ligand-supported clusters exists, such as the heidi-

bound versions of the **Ga_{13}** and **Al_{13}** clusters that were described in Chapter I, which have a triply-deprotonated heidi ligand that replaces three of the H_2O ligands on each of the six peripheral gallium or aluminum ions, as well as one of the hydroxide bridges.[10,16,17] Also discussed in Chapter I is the general lack of larger nuclearity metal hydroxide clusters isolated without stabilization by organic ligands. It is known that in the case of Keggin-Al_{13}, water ligands bound to the octahedral aluminum atoms can be substituted by various phenol-based ligands, which eventually causes decomposition of the cluster.[9] This is due to the presence of only one water ligand per aluminum atom in Keggin-Al_{13}. A bidentate ligand replaces the water ligand upon formation of the initial bond, and then causes breakage of a hydroxide bridge bond with formation of the second phenolate-aluminum bond. Decomposition of the entire cluster occurs rapidly thereafter. An even number of water ligands per metal center in our M_{13} clusters should decrease the likelihood of this occurrence.

Ligand substitution is a worthwhile area of exploration for several reasons. First, the choice of peripheral ligands is usually dictated by which ligands facilitate cluster formation. In our case, the all-inorganic clusters with only H_2O ligands on the outer ring metal ions are readily available, giving the opportunity to tailor ligand choice according to which ligands interest us, not simply which nucleate or template cluster growth. The ability to choose supporting ligands gives control over the properties and functionality exhibited by the clusters. The appropriate ligand could impose different solubility properties by altering the charge of the cluster or adding aliphatic content. Reactivity could also be imparted, such as a case involving substitution by a bidentate ligand

containing two olefin groups, which could undergo olefin metathesis with neighboring ligands to generate a large macrocycle surrounding the M_{13} core (Figure 5.4).

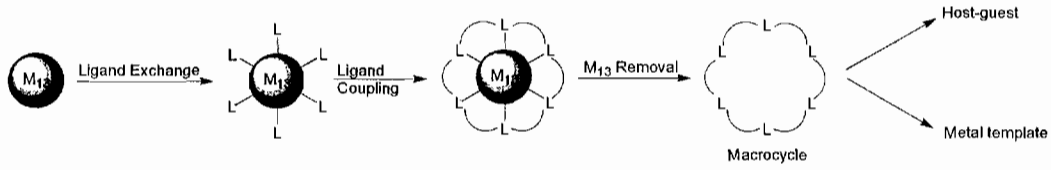


Figure 5.4. Functionalization of M_{13} compound with organic ligands. In this idealized situation, organic ligands would bind to a M_{13} core. The ligands would then be coupled together using additional chemistry, followed by hydrolysis or another process to remove the metal core, affording a large macrocycle.

Functionalization of M_{13} clusters with appropriate ligands may facilitate self-assembly onto solid supports as well. For example, one could imagine assembling a monolayer of single-molecule magnets on a surface of interest by functionalizing them with appropriate ligands to bind to the surface. Additionally, a multidentate ligand may facilitate the synthesis and isolation of higher order structures. With aluminum and non-Group 13 metals such as iron and manganese, clusters with 15 and 19 metal ions are known in ligand-supported forms. In these cases, ligands with a high coordination number are often used, such as H_3heidi or H_5hpdta.[10,18] The addition of a ligand such as these to our tridecameric clusters may help isolate larger species.

Ligand exchange reactions could prove useful in the research area of mineral mimics as well. Aluminum oxo/hydroxo clusters have been touted as natural mineral mimics, but there is limited research supporting this claim due to the general synthetic inaccessibility of such clusters.[5,6] Mimics are useful because precise characterization of

bulk minerals can prove difficult. This can be likened to protein research, where small-molecule active site mimics are often synthesized to gain better understanding of the native protein. In this example, M_{13} clusters are the potential active site mimic, and natural minerals constitute the native protein. In one example of mineral ligand exchange, Barron et al. show that the mineral boehmite (AlO(OH)) can be functionalized with molecules such as benzoic acid.[11] Gallium and aluminum have been shown to exhibit parallel hydrolytic behavior, so the observation of a similar functionalization of **Ga_{13}** or **Al_{13}** with organic ligands such as benzoic acid would provide experimental evidence of M_{13} mineral mimicry. It is conceivable that the M_{13} clusters could act like a large single metal ion, a bulk mineral, or something different.

Heterogeneous Ligand Exchange

My first attempt at ligand exchange utilized a heterogeneous approach. Finely ground crystals of **Ga_{13}** were suspended in an organic solvent (typically an aromatic hydrocarbon) in which potential ligands were dissolved. The first solvent system explored was *p*-xylene, due to its high boiling point. A number of organic ligands including benzoic acid, toluic acid, malonic acid, and 2,2'-bipyridine were added to the suspension containing solid **Ga_{13}**. Control reactions with no ligand present were also set up. In *p*-xylene, reactions were generally heated for 24 hours at 120 °C. Upon cooling, it was noted that the solutions had developed a yellow color and contained a powdery solid. There was also the distinct smell of an aromatic aldehyde after the heating period.

Because a single-crystalline product was not obtained, NMR analysis was used to analyze the resultant reaction mixtures. NMR spectra of the solid and liquid products recovered from the *p*-xylene solvent showed a complicated series of peaks (Figure 5.5). It was noted that the spectra showed peaks possibly corresponding to a carboxylic acid, an aldehyde, and up to 23 peaks of varying intensity between 4 and 5.5 ppm. A number of control reactions run without ligands present in various solvents (*p*-xylene, toluene, and hexadecane) showed similar oxidation behavior. Control reactions run with $Ga(NO_3)_3$, $In(NO_3)_3$, and KNO_3 in the absence of ligands resulted in similar NMR spectra exhibiting peaks corresponding to oxidation products, though with different peak intensities ($Ga(NO_3)_3$ is shown in Figure 5.5). Using gas chromatography-mass spectroscopy (GC/MS) it was determined the solution originally containing $\mathbf{Ga_{13}}$ and *p*-xylene still contained mostly *p*-xylene (55 %), but also *p*-tolualdehyde (15 %) and *p*-toluic acid (5 %), in addition to other lesser products. From these data, it was hypothesized that *p*-xylene was being oxidized (presumably by molecular oxygen) into these various products. Degassed reactions run under nitrogen exhibited much smaller peaks corresponding to the oxidation products, supporting the hypothesis that molecular oxygen plays a role in the observed oxidations, with activation by the $\mathbf{Ga_{13}}$ compound.

In hopes of avoiding this oxidation side reaction, a variety of solvents were examined in place of *p*-xylene, as it appeared too susceptible to oxidation. Solvents such as benzene, toluene, 1,1,2,2-tetrachloroethane, nitrobenzene, hexadecane, and liquid CO_2 failed to yield concrete, characterizable results. Neat reactions were run, either by heating benzoic acid to above its melting point with $\mathbf{Ga_{13}}$ present, or using benzyl alcohol

as a solvent/ligand combination. Similar to *p*-xylene, NMR spectra suggested the oxidation of toluene and hexadecane. The other solvents tested failed to yield positive results as well. A wide variety of potential ligands were tested, including nitrilotriacetic acid disodium, toluic acid, malonic acid, and 2,2`-bipyridine. When 2,2`-bipyridine was used, new peaks shifted downfield appeared, but these were shown to correspond to protonated ligand, not a gallium-bipy complex.

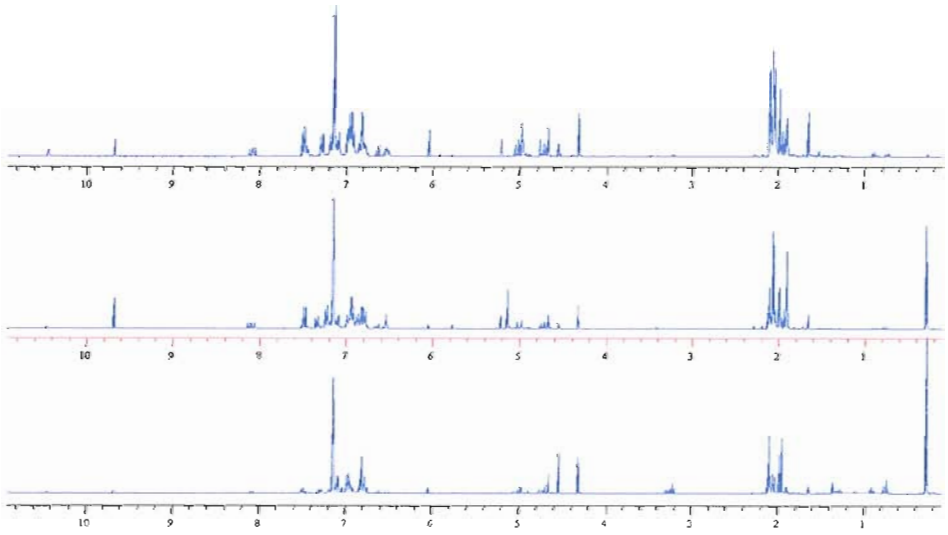


Figure 5.5. NMR spectra from ligand exchange reactions. The top spectrum corresponds to $\mathbf{Ga_{13}}$ heated with *p*-xylene, open to air. Note appearance of peaks in aldehyde and carboxylic acid range. The middle spectrum represents $Ga(NO_3)_3$ with *p*-xylene. Similar peaks appear in this spectrum as with $\mathbf{Ga_{13}}$. The bottom spectrum shows $\mathbf{Ga_{13}}$ with *p*-xylene under reduced oxygen conditions. The reaction was degassed and kept under nitrogen atmosphere. The size of the apparent aldehyde and carboxylic acid peaks are much reduced, suggesting molecular oxygen plays a role in the reaction.

Reflecting on these results following a helpful discussion with Dr. Lev Zakharov, it was determined that due to tight crystal packing there is most likely not enough space between $\mathbf{Ga_{13}}$ clusters in the solid state to allow ligand substitution. It is possible that ligands on the surface of the crystals were substituted, but these represent only a small portion of the total clusters present and leave the rest with H_2O ligands or decomposed due to heating. Powder X-ray diffraction of the powder isolated after the reactions showed no diffraction peaks, but it is suspected to be a dehydrated form of gallium, such as Ga_2O_3, GaO(OH), or $Ga(OH)_3$. Important conclusions from these studies include the notion that solid phase ligand exchange is unlikely to yield successful ligand exchange results. However, the potential catalytic behavior of $\mathbf{Ga_{13}}$ toward the oxidation of *p*-xylene and other solvents with molecular oxygen might be an interesting follow-up study, especially if this activation can be performed selectively.

Homogeneous Ligand Exchange

Experiments utilizing homogenous ligand exchange ($\mathbf{Ga_{13}}$ and potential ligand dissolved in the same solution) were performed using a variety of different ligands. $\mathbf{Ga_{13}}$ is known to dissolve in MeOH, H_2O, ethylene glycol, and propylene glycol (and perhaps to a small degree in diethylene glycol, though not in butylene glycol or any of the other highly polar organic solvents tested). This solvent variety provides a starting point for solution phase ligand substitution. Propylene and ethylene glycol are themselves potential ligands; if either of these molecules replace water ligands, it may drastically

alter the solubility of **Ga_{13}** by changing the charge of the molecule and adding aliphatic content. Dissolution in either ethylene or propylene glycol was followed by recrystallization attempts through vapor diffusion of various solvents. With ethylene glycol solutions, isopropyl alcohol, acetone, tetrahydrofuran, and 1,4-dioxane were used as diffusion solvents; isopropyl alcohol was used as a diffusion solvent with propylene glycol solutions. None of these recrystallization attempts yielded crystalline product. Similar attempts were made with diethylene glycol, butylene glycol, propanedithiol, and ethylenediamine. No appreciable amount of **Ga_{13}** dissolved in any of the solvents; rigorous stirring only resulted in additional breakup of the **Ga_{13}** crystals.

In addition to the ligand exchange reactions where the solvent was a potential ligand itself, other homogeneous **Ga_{13}**/ligand substitutions were screened. Ligands used for these potential transformations included 2,2'-bipyridine, 4-aminobenzoic acid, catechol, H_3heidi, nitrilotriacetic acid, and thiosalicylic acid. Generally, twelve equivalents of the ligand were added for each equivalent of **Ga_{13}**, though in the case of H_3heidi, only six equivalents were added and in the case of 4-aminobenzoic acid 50 equivalents were added. Only six equivalents of H_3heidi were deemed necessary based on the stoichiometries of Ga_{13}heidi$_6$ and Al_{13}heidi$_6$ compounds previously reported in the literature.[10,17,19] H_3heidi was dissolved in MeOH with **Ga_{13}** and a small amount of pyridine to deprotonate the ligand, although such a base was not added during the screening of other potential ligands.[10] In the case of H_3heidi ligand, this procedure afforded an insoluble precipitate, which could not be redissolved. With catechol, the first attempt at ligand substitution was not performed under air-free conditions. This was later

thought to lead to decomposition of the ligand, so additional attempts utilized air-free techniques and were run under argon.[9] Multiple recrystallization attempts with these different potential ligands did not yield a crystalline product. NMR characterization did not suggest coordination of new ligands either.

Biphasic Ligand Exchange

Beyond homogeneous and heterogeneous ligand exchange methods, a biphasic approach was examined. In biphasic ligand exchange, the $\mathbf{Ga_{13}}$ clusters and potential ligands were dissolved in various solvents, which were then vigorously mixed in order to facilitate transfer between the different solvent layers. Biphasic reactions are of interest because they eliminate the need for ligand and $\mathbf{Ga_{13}}$ co-solubility, which expands ligand choice. Consequently, a number of conditions were screened using a biphasic ligand exchange approach. *N*,*N*-dimethyl-4-nitrosoaniline was chosen due to its highly colored nature and known affinity for Ga(III). As a result, any ligand transfer to the $\mathbf{Ga_{13}}$ layer should be readily evident. It was found that some color transfer occurred even in control reactions, and no crystalline product was isolated. Reactions run with terephthalic acid yielded similar results, with no crystalline product.

Conclusion

Previous reports (such as those summarized in Chapter I) have shown that metal hydroxide nanoclusters are often isolated when stabilized by exterior ligands, so precedence for ligand-supported clusters certainly exists.[10,17-22] Additionally, substitution of H_2O ligands has been shown in Keggin-Al_{13} clusters.[9] It seems reasonable that the correct conditions must simply be found to substitute and re-isolate ligand-substituted M_{13} clusters such as $Ga_{13}L_x$ or $Al_{13}L_x$ (L = any potential ligand bound to the tridecameric clusters). Initial attempts to utilize a heterogeneous method proved unsuccessful, most likely due to lack of access to the proposed exchange sites because of tight crystal packing. Attempts at homogeneous and biphasic ligand exchange have also proven less than fruitful. Given this finding, there are several future research questions that apply to the area of ligand exchange.

Are H_2O ligands exchangeable under homogenous conditions? Based on the heterogeneous ligand exchange attempts, it appears that in order for all H_2O ligands to be replaced (or at least some on all clusters) the clusters must be dissolved in order to be accessible to potential ligands. **Ga_{13}** is soluble in H_2O, MeOH, ethylene glycol, and propylene glycol. Each of these solvents is a potential ligand candidate itself, with the latter two being the most interesting due to their potential bidentate chelating nature. Bidentate ligands are preferable to monodentate to slow the rate of ligand exchange on the gallium ions. Therefore, future exploration in this area would likely focus on bidentate, polar molecules, such as catechol and salicylic acid. If a bidentate ligand can

be shown to bind to **Ga_{13}**, it could be exploited for macrocycle applications described in the ligand exchange introduction (Figure 5.4).

Will biphasic conditions facilitate H_2O ligand exchange? The potential ligands are currently limited to those soluble in solvents that dissolve **Ga_{13}**, so a biphasic exchange might prove useful. This way, any organic soluble ligand could be used. **Ga_{13}** could be dissolved in a suitable solvent (most likely H_2O or MeOH) and layered with an organic solution containing the appropriate ligand followed by vigorous stirring to mix the layers. In this case, fluorescent or colored ligands could be used, enabling visual confirmation of ligand substitution by tracking transfer of color from one solvent to the next. A color shift or fluorescence quenching may be observed upon binding to **Ga_{13}**, providing ease of characterization.

*Can **Ga_{13}** or other M_{13} act as a metal template for large macrocycles?* Ligand substitution might open the door for future metal-templated reactions. By exchanging H_2O ligands for a predesigned ligand containing two reactive groups in close proximity to each other, then reacting the bi-functional ligand with another on an adjacent gallium ion, a large, continuous ligand shell encircling the cluster could be formed. By etching the cluster or protonating the ligand, a large macrocycle could subsequently be generated. One potential class of ligands to use in such experiments would be a bi-functional weak-strong binding ligand with two olefin moieties. Once bound to adjacent gallium or indium ions, olefin metathesis could be performed to link the ligands and form a macrocycle. This macrocycle could itself possess interesting properties (similar to cucurbituril or cyclodextrin), and could be used to template synthesis of other metal

clusters (Figure 5.4). A macrocycle made in this manner would be expected to be high-yielding and monodisperse, as the number of ligands being coupled to form the macrocycle would be predetermined by the number of ligands bound to the cluster.

There are plenty of potential experiments to run with regard to metal exchange as well. As mentioned, computational experiments might be beneficial to determine what metal ions would favorably replace gallium atoms. A rigorous test of different pH conditions might prove fruitful with some of the different metal ions, though a balance must be found where the clusters remain sufficiently intact but hydroxide bridges can be formed to bridge additional metal ions.

Bridge to Chapter VI

We have demonstrated the successful synthesis of a variety of tridecameric hydroxide clusters, from homometallic **Ga_{13}** and **Al_{13}** to heterometallic Ga/In and Al/In clusters. We have isolated ten compounds in total so far, and have attempted to isolate other compounds through metal and ligand exchange reactions. In the process of trying to isolate additional compounds such as In_{13} and heterometallic compounds containing non-Group 13 metals, we have isolated several other examples of compounds containing Group 13 metal ions. Four of these compounds will be discussed in Chapter VI; two containing gallium, one with indium, and one with aluminum.

CHAPTER VI

ISOLATION OF TWO ADDITIONAL CLASSES OF GROUP 13-CONTAINING MOLECULES

Introduction

During the course of the projects described in the preceding chapters, several more Group 13 containing structures were isolated, including Ga- and In-acetate 1-D chains and Anderson molybdate clusters with the central metal substituted by gallium or aluminum. The chain structures were produced by a similar technique to the tridecameric clusters featured in Chapters II-V, with ethyl acetate hydrolysis supplying the acetate groups. Two unusual complexes of formula $[M(\mu\text{-}OH)(\mu\text{-}O_2CCH_3)_2]_n$ (M = In or Ga) were crystallized by diffusion of ethyl acetate into methanolic solutions of the $M(NO_3)_3$ salts and *N*-nitrosopyrrolidine (Scheme 6.1). These represent the first examples of such simple 1-D chains comprising Group 13 elements, and their formation results from the surprising hydrolysis of ethyl acetate to provide the bridging acetate ligands. These structures were synthesized and isolated by myself with single-crystal X-ray characterization by Dr. Lev Zakharov. The principal investigator for this research was Prof. Darren W. Johnson, who also provided editorial assistance. The results of these

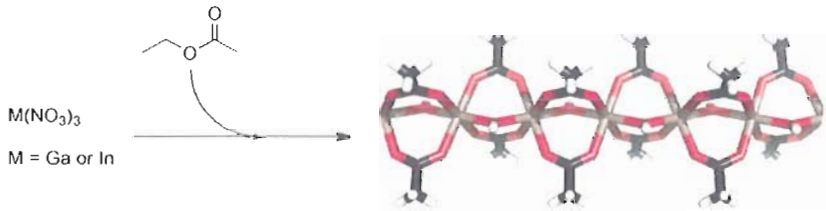
studies were published in volume 48 of *Inorganic Chemistry*, a publication of the American Chemical Society, in March 2009.[1]

The second set of results detailed will be the synthesis of gallium- and aluminum-centered Anderson-type molybdate clusters. In this case, the synthesis and isolation were again performed by myself, with single-crystal X-ray characterization performed by Dr. Lev Zakharov. The principal investigator was Prof. Darren W. Johnson, who provided editorial assistance. The results of this study were published in *Acta Crystallographica Section E*, a publication of the International Union of Crystallography.[2]

Interest in Infinite Group 13 Networks

Interest in the area of infinite Group 13 carboxylate compounds originates from several areas, stimulated largely by work on metal-organic frameworks (MOFs) and zeolites.[3-7] Numerous examples of 1-D, 2-D, and 3-D indium (and fewer of gallium) carboxylate extended structures exist, often taking advantage of benzene di- and tricarboxylates as bridging ligands between metal centers.[8-17] In these cases, ligand geometry seems to have a dominant effect on the final extended structure.[12] However, the steric bulk of the bridging ligands also plays a role, with *t*-butyl or other bulky ligands often forming rings instead of chains.[18,19] One structure type was notably absent from this literature—a truly one-dimensional chain of gallium or indium with bridging acetate and hydroxide—a surprising omission given the interest in chain structures comprising Group 13 elements.[20-22]

In addition to the multi-dimensional extended indium structures mentioned above, there are examples of non-linear or extended discrete structures of Group 13 ions, such as an elegant "gallic wheel" produced by Christou and coworkers.[19] The metal ions in these gallic wheel and indium carboxylate structures possess similar coordination environments to the 1-D chain structures presented in this chapter, but form more complicated extended structures.[14,15] Several additional reports have detailed a related manganese 1-D chain structure, which is the only other example of this infinite linear chain topology with acetate and hydroxide I have encountered.[23-26] A recent report describes a structure similar to the indium chain, but with iodate bridging ligands in place of acetate.[27]



Scheme 6.1. General synthetic route to 1-D acetate chain compounds. Gallium or indium nitrate are combined in methanolic solution with *N*-nitrosopyrrolidine, which is allowed to evaporate, then ethyl acetate is added via vapor diffusion. After several months, single-crystalline product of **In-chain** and **Ga-chain** are isolated.

In this chapter two new infinite chain structures of formula $[In(\mu\text{-}OH)(\mu\text{-}O_2CCH_3)_2]_n$ (**In-chain**, Figure 6.1) and $([Ga(\mu\text{-}OH)(\mu\text{-}O_2CCH_3)_2]\cdot HOAc\cdot H_2O)_n$ (**Ga-chain**, Figure 6.2) are described. To the best of my knowledge, the **In-chain** and **Ga-chain** structures are the first examples of such acetate-hydroxy bridged chain compounds

comprising Group 13 metals, and also showcase an interesting reaction wherein ethyl acetate is hydrolyzed, then incorporated as acetate in the resulting structures.

Synthetic Procedure for 1-D Chains

These compounds were discovered during investigation of the tridecameric Group 13 hydroxo/aquo nanoclusters such as **Ga_{13}**, **Al_{13}**, and **Ga_7In_6**, which I described in Chapters II, III, and IV.[28-30] During my efforts to isolate an analogous In_{13} structure (which has remained elusive), I instead isolated the indium chain compound **In-chain** (Figure 6.1). The same methodology was successfully applied to isolate the gallium chain structure **Ga-chain** (Figure 6.2). $M(NO_3)_3$ salts (M = Ga or In, 1 equiv.) were dissolved in methanol, then *N*-nitrosopyrrolidine (1.85 equiv.) was added, affording a clear yellow tinted solution. HPLC grade methanol was obtained from J.T. Baker and used without further purification (water content < 0.1%). No attempt was made to keep the methanol anhydrous. Hydrated metal nitrate salts were also used, so all the water necessary for incorporation as hydroxide bridges was available from these salts, water in the solvent, and other adventitious water. The methanolic solutions were evaporated open to air at room temperature, giving a viscous yellow solution. The vials were then sealed in jars containing ethyl acetate (~20 mL) to allow for vapor diffusion into the yellow solution. After several months, crystals suitable for single-crystal X-ray diffraction formed, revealing the **In-chain** and **Ga-chain** structures, respectively. **In-chain** was also isolated with di-*n*-butylnitrosamine replacing *N*-nitrosopyrrolidine.

However, using di-*n*-butylnitrosamine with $Ga(NO_3)_3$ produces **Ga_{13}** instead.[30] Interestingly, when the same conditions are applied to $Fe(NO_3)_3$, an iron trimer (well-known in the literature) is isolated instead of a chain structure.[31,32]

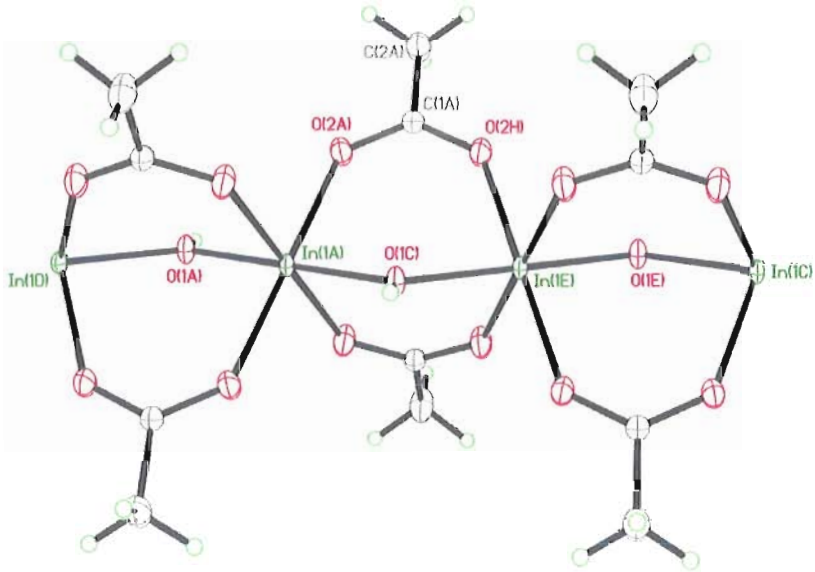


Figure 6.1. Ortep visualization (50 % probability) of In-acetate 1-D chain compound. The structural details present in the solid state can be seen in the above figure. Indium atoms are octahedral and bound to four acetate bridges and two hydroxide bridges. This structural morphology continues to form an infinite one-dimensional chain compound.

Structural Description of Chain Molecules

In-chain and **Ga-chain** consist of infinite linear chains of bridged metal ions (Figure 6.1). Each trivalent octahedral metal ion is bound to two μ-OH groups and four μ-1,3-OAc ligands. These are shared with neighboring metal ions, giving a formula of

$[M(\mu\text{-}OH)(O_2CCH_3)_2]_n$, which results in an overall neutral charge. Interestingly, no interstitial molecules are present in **In-chain** and neighboring chain molecules show little intermolecular interaction. Many examples of Group 13-carboxylate structures contain interstitial molecules, so it is unusual that chain structure **In-chain** lacks such solvent molecules.[8,10,11,13-15,27]

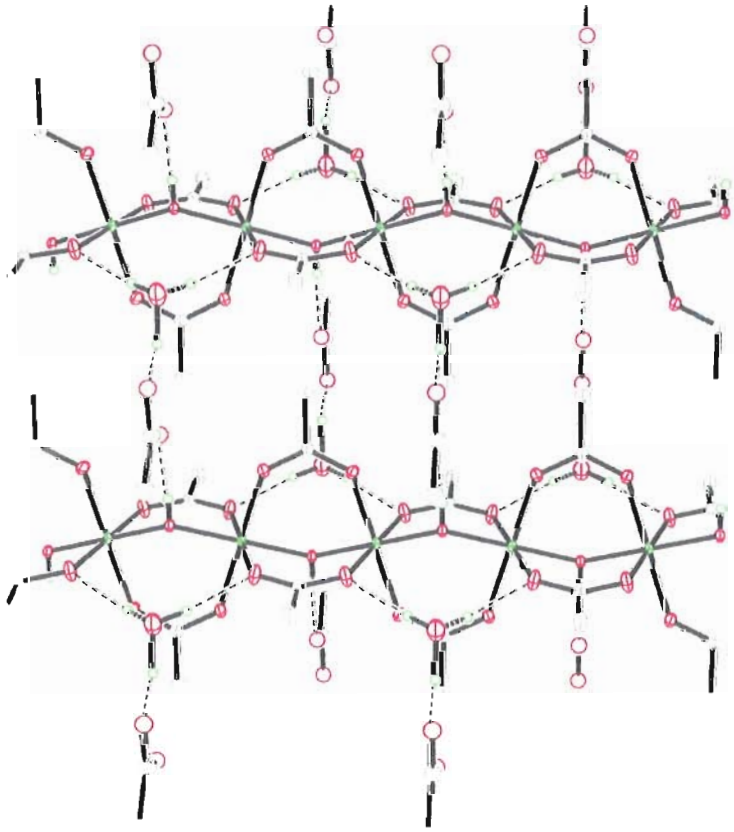


Figure 6.2. Ortep representation (50 % probability) of the crystal structure of the gallium 1-D chain compound. This crystal structure features the presence of interstitial molecules of water and acetic acid. These interstitial molecules hydrogen bond to each other and to the chain molecules.

Unlike the indium chain, the gallium chain contains acetic acid and water in the interstitial space between chains (Figure 6.2). As with the μ-1,3-OAc bridging ligands, acetic acid solvent is also derived from the hydrolysis of ethyl acetate. Acetic acid and water form a network of interchain hydrogen bonds throughout **Ga-chain** (Figure 6.2). Acetic acid hydrogen bonds to the hydroxyl bridges and water molecules, while the water molecules hydrogen bond with the interstitial acetic acid and the oxygen atoms of the acetate bridges. The acetic acid and water molecules in **Ga-chain** are disordered over two positions related by a mirror plane. A similar network of hydrogen bonds, but without the disorder, is found in the structure of the previously reported manganese chain.[25]

The presence of water and acetic acid in **Ga-chain**, but not in **In-chain** can be rationalized in two ways. Gallium has a higher Lewis acidity than indium, and is therefore more likely to hydrolyze ethyl acetate, giving acetate or acetic acid. This may produce a higher acetate concentration in the crystallization solution. Gallium also has a smaller atomic radius than indium, which may leave more space in the crystal structure for incorporation of interstitial water and acetic acid.

Hydrolysis of Ethyl Acetate

As mentioned, the origin of the acetate bridges, derived from the hydrolysis of ethyl acetate, is also of interest in these structures. Ethyl acetate is hydrolyzed and incorporated into the chain structures in two different ways: as bridging acetate ligands

and as acetic acid in the interstitial spaces. Traditionally, extended structures bearing carboxylate ligands introduce the carboxylate moiety directly, e.g., as benzene carboxylates or sodium acetate. However, in a related example, Borovik and co-workers have described a case of mild ethyl acetate hydrolysis and acetonitrile hydration followed by structural incorporation of acetate and acetamidate ligands.[33] In this structure, the acetate moiety occupies a 1,3-bridging position between two cobalt(II) ions while hydrogen bonding with urea groups, similar to the binding motif seen in the gallium chain structure where acetate oxygen atoms hydrogen bond to water molecules. Borovik was also able to isolate the same structure by direct treatment with an acetate source, whereas we have yet to isolate the chain structures by such means or in the absence of the nitroso compound.

Conclusion to Group 13 Chain Compounds

The application of indium and gallium in organic transformations has been widely studied, with a range of transformation types examined, but reviews of the topic do not discuss hydrolysis reactions.[34-37] Nevertheless, these observations suggest that indium and gallium hydroxide complexes may be worth exploring as mild reagents for hydrolysis activation. For instance, in this report up to three acetates are formed per metal ion based on the stoichiometry found in the crystals, and the crystallization vials also smell of acetic acid, providing further support of ester hydrolysis using Group 13 metals.[37]

Furthermore, it may be possible to use such an approach in the hydration of other molecules such as acetonitrile, as demonstrated by Borovik and co-workers.[33]

Summary of Crystallographic Data

Crystal data for $C_4H_7InO_5$ ***(Ga-chain)***: M_r = 249.92, colorless block, 0.34 × 0.18 × 0.09 mm, orthorhombic, space group *Cmcm*, T = 173 K, MoK$_\alpha$ (0.71703 Å), a = 14.570(5) Å, b = 6.831(2) Å, c = 7.269(2) Å, V = 723.5(4) Å^3, Z = 4, ρ_{calcd} = 2.294 g/cm^3, μ = 3.23 mm^{-1}, F(000) = 480, $2\theta_{max}$ = 56.5°, 1962 reflections collected, 481unique [R_{int} = 0.011]. R indices [$I > 2\sigma(I)$]: R1 = 0.0167, wR2 = 0.0475, GOF = 1.131.

Crystal data for $C_6H_{13}GaO_8$ ***(In-chain)***: M_r = 282.88, colorless block, 0.28 × 0.08 × 0.05 mm, monoclinic, space group *P*2(1)/*m*, T = 173 K, MoK$_\alpha$ (0.71703 Å), a = 7.9516(7) Å, b = 6.7651(6) Å, c = 10.6719(10) Å, β = 106.1500(10)°, V = 551.42(9) Å^3, Z = 2, ρ_{calcd} = 1.704 g/cm^3, μ = 2.52 mm^{-1}, F(000) = 288, $2\theta_{max}$ = 54.0°, 6194 reflections collected, 1302 unique [R_{int} = 0.024]. R indices [$I > 2\sigma(I)$]: R1 = 0.0304, wR2 = 0.0782, GOF = 1.106.

Description of Anderson Clusters

Anderson first described a planar polyanion in 1937.[38] Anderson-type clusters (as they are now known) are well established and many papers detailing their preparation and applications have been published.[39,40] Compounds containing Anderson-type clusters

have been explored for applications as structural aesthetics, biologically active compounds, and catalysts.[39] They have also been shown to function as building blocks for larger molecular assemblies, where they can be linked to form extended networks with pores and cavities.[41,42] The majority of Anderson clusters are based on $Mo_7O_{24}^{6-}$ or $W_7O_{24}^{6-}$ frameworks, and many structures have been synthesized with substitution of the central octahedron or variable bridging ligands. A similar planar arrangement of seven metals is observed at the core of the recently reported structure of $[Ga_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$.[28] Attempts to synthesize derivatives of this compound led to isolation of $(NH_4)_3[Ga(\mu_3\text{-}OH)_6Mo_6O_{18}]\cdot 7H_2O$ (**GaMo$_6$**) and $(NH_4)_3[Al(\mu_3\text{-}OH)_6Mo_6O_{18}]\cdot nH_2O$ (**AlMo$_6$**) compounds that are described in the following pages.[2]

Extensive literature reports have covered the different structural variants and chemistry of hexamolybdoaluminate(III) polyanions.[39] The gallium-substituted B-type Anderson compound has been synthesized previously, by adding a solution of gallium metal in concentrated HNO_3 to a solution of MoO_3 in aqueous NaOH.[43,44] The mixture was heated overnight and rinsed several times with acetone, and vacuum dried overnight, affording product as the sodium salt. However, a crystal structure determination of **GaMo$_6$** had not been reported.[44] Synthesis by the metal exchange method reported in this chapter represents a far more benign method than that previously reported.[44] The synthesis reported herein also represents an alternative preparation of the Al-substituted structure, with no acid addition required (as is usually the case). There are several literature reports of this structure, so the focus of this section is on **GaMo$_6$**.

Synthetic Preparation of Substituted Anderson Clusters

Due to the similarity of the structure of the $Mo_7O_{24}^{6-}$ complex to the inner planar core of the reported **Ga_{13}** metal hydroxide cluster $[Ga_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$, it was hypothesized that a heterometallic Mo_7Ga_6 compound might be obtained by reaction of $(NH_4)_6Mo_7O_{24}$ with six or more equivalents of $Ga(NO_3)_3$.[28] Setting up the reaction in a similar manner to the synthesis of **Ga_{13}** (dissolving starting materials in a MeOH:H_2O mixture and adding di-*n*-butylnitrosamine), provided single crystals of the gallium-substituted B-type Anderson cluster, $(NH_4)_3[Ga(\mu_3\text{-}OH)_6Mo_6O_{18}]\cdot 7H_2O$, (**$GaMo_6$**), which were isolated and structurally characterized by X-ray crystallography (Figure 6.3).[2]

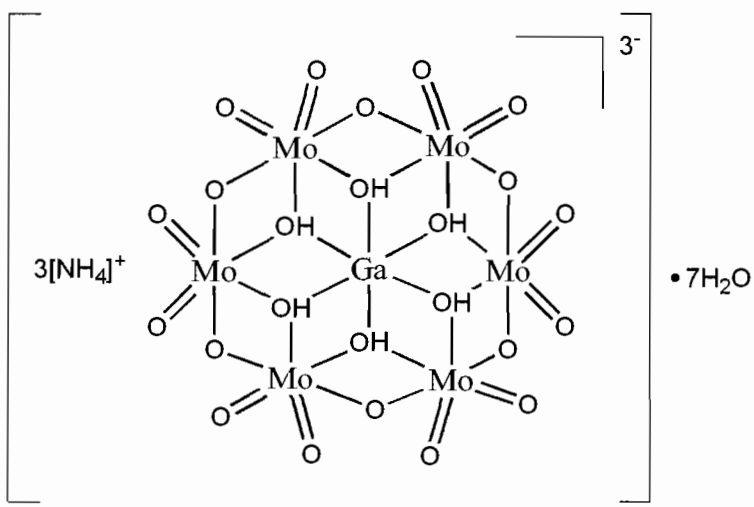


Figure 6.3. ChemDraw representation of the $GaMo_6$ anion. This structure has a molecular formula of $(NH_4)_3[Ga(\mu_3\text{-}OH)_6Mo_6O_{18}]\cdot 7H_2O$. The $[Mo_7O_{24}]$ starting material has a -6 charge which decreases to a -3 charge upon protonation of the six μ_3-oxide bridges, as well as the substitution of Ga(III) for Mo(VI).

Commercial products $(NH_4)_6Mo_7O_{24}$ (Baker and Adamson) and $Ga(NO_3)_3 \cdot nH_2O$ (Strem) were used to obtain **$GaMo_6$**. $(NH_4)_6Mo_7O_{24}$ (0.25 g, 0.2 mmol) and $Ga(NO_3)_3$ (0.7 g, 1.92 mmol) were dissolved in a 1:1 H_2O/MeOH mixture (10 mL) in a 20 mL scintillation vial. The mixture was heated slightly (while open to atmosphere in a fume hood), with some cloudiness remaining in the mixture. Di-*n*-butylnitrosamine (0.45 g, 0.5 mL, 2.8 mmol) was added, and was not initially miscible. Additional MeOH (~2 mL) brought most into solution, and the mixture was then filtered. The remaining solution was evaporated, and after 9 days clear, colorless crystals with block-like habit had formed around the outside edge of the vial. The crystals were isolated in 90 % crude yield. Fewer equivalents of $Ga(NO_3)_3$ (relative to $(NH_4)_6Mo_7O_{24}$) and no organic additive (H_2O as solvent only) were also used successfully to produce crystals of **$GaMo_6$**.[2] **$AlMo_6$** is synthesized in a similar manner, simply substituting $Al(NO_3)_3 \cdot 9H_2O$ for $Ga(NO_3)_3 \cdot nH_2O$.

Crystallographic Details

The planar structure consisting of seven metals observed in the parent Anderson compound is also present in the structure of **$GaMo_6$**, with average Ga—O bond lengths of 1.97 (1) Å. The crystal structure of $(NH_4)_3[GaMo_6(OH)_6O_{18}] \cdot 7H_2O$, contains two centrosymmetric **$GaMo_6$** B-type Anderson cluster units consisting of central GaO_6 octahedra surrounded by a hexagonal assembly of MoO_6 edge-sharing octahedra (Figures 6.4 and 6.5). Like other B-type Anderson clusters where the central Mo atom is

substituted with a di- or trivalent metal ion, the central six μ_3-oxido bridges are protonated.[39] There are six μ_3-OH bridges, six μ-oxo bridges, and twelve terminal oxo ligands for each of the two independent cluster anions (Figure 6.4). The average Ga–O bond length is 1.97(1) Å, whereas the average Mo–O distances are 2.29(2), 1.94(1) and 1.709(5) Å, respectively, for Mo–(μ_3-OH), Mo–(μ-O), and Mo=O bonds. In the crystal structure, the $Ga(\mu_3\text{-}OH)_6Mo_6O_{18}^{3-}$ polyanionic clusters are surrounded by NH_4^+ cations and solvent water molecules, forming an extended network of hydrogen bonds.

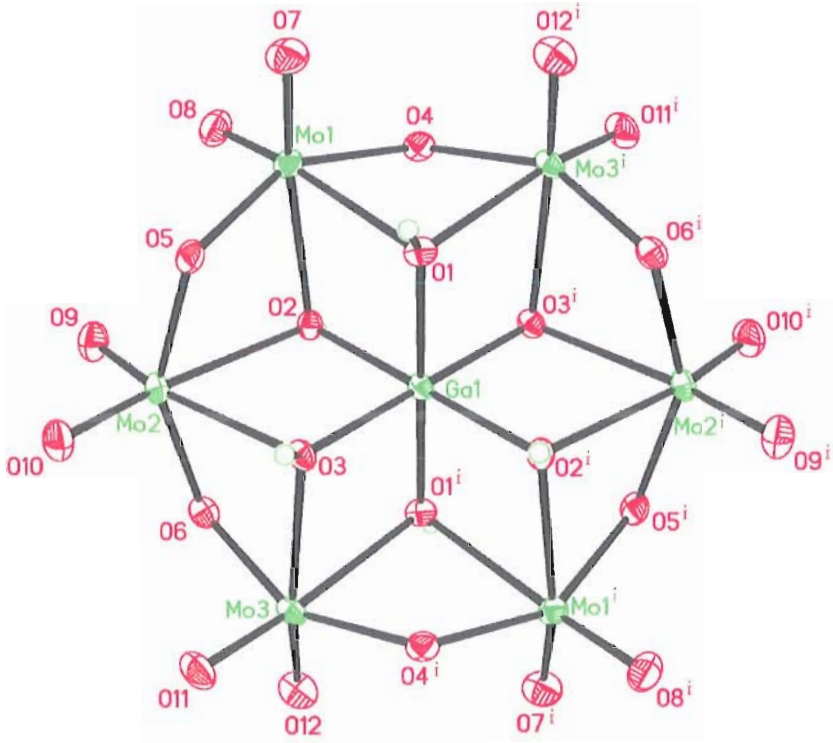


Figure 6.4. One of the two symmetrically independent $GaMo_6$ clusters in the crystal structure of $GaMo_6$. Displacement ellipsoids are drawn at the 50 % probability level (symmetry code (i): i – x, i – y, i – z).

The hydrogen atoms of the μ_3-oxo groups were found from difference Fourier maps and were refined with restraints; the value of 0.85 Å was used as a target for corresponding O–H distances in the refinement. The hydrogen atoms in the NH_4^+ cations and solvent water molecules were not found and thus were not taken into consideration. Positions of nitrogen atoms of the NH_4^+ cations versus positions of the solvent water molecules were found based on analysis of the network of hydrogen bonds

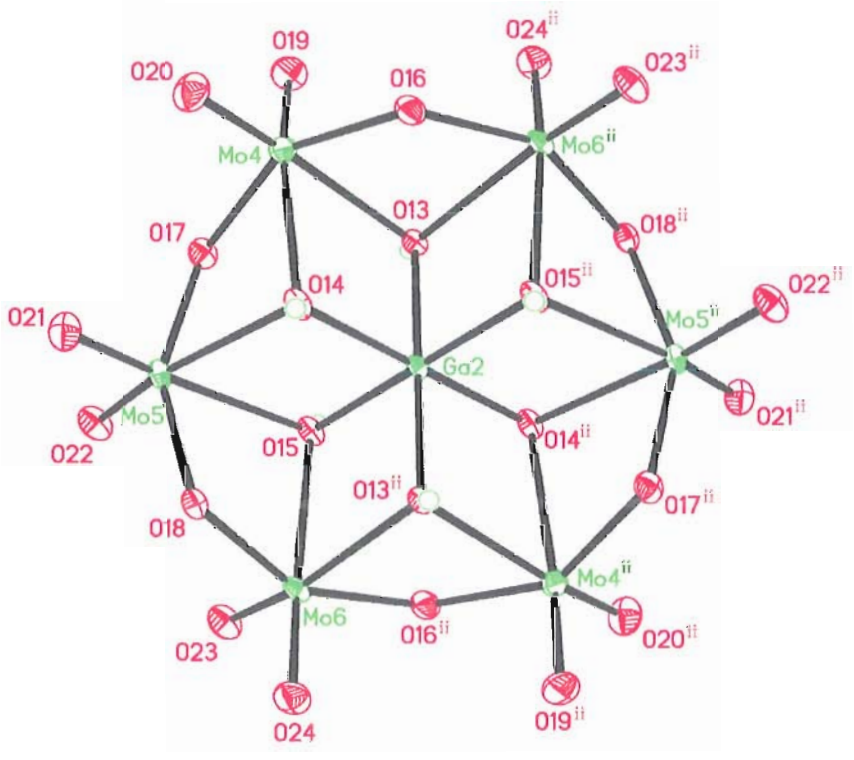


Figure 6.5. The second polyanionic cluster present in the crystal structure of $GaMo_6$. This ortep representation is at the probability level of 50 %. The symmetry code for this cluster is – x, 1 – y, 1 – z.

in the structure. The positions of two NH_4^+ cations found in the structure of **$GaMo_6$** are close to positions of the K^+ cations found in the structure of $K_3[Co(\mu_3$-

$OH)_6Mo_6O_{18}]\cdot 7H_2O$, but the position of the third one is different compared to the positions of the third K^+ cation in the potassium compound. Both structures crystallize in the same space group and exhibit similar lattice parameters. However, the β-angles in these structures are different (100.212 (1)° in **GaMo$_6$** *versus* 94.577 (9)° in $K_3[Co(\mu_3$-$OH)_6Mo_6O_{18}]\cdot 7H_2O$) which indicates the packing in these structures seems to be different.[40] The highest peak and the deepest hole observed in the final Fourier map are 0.96 and 0.87 Å away from atoms O1S and Mo6, respectively.

Crystal data for $H_{32}GaMo_6N_3O_{31}$ (***GaMo$_6$***): T = 173 (2) K, MoK_α (0.71073 Å), Mr = 1215.65, colorless plates, 0.38 × 0.20 × 0.03 mm, monoclinic, space group $P2_1/c$, a = 22.7642 (15) Å, b = 10.9651 (7) Å, c = 11.7599 (8) Å, β = 100.2120 (10)°, V = 2888.9 (3) Å^3, Z = 4, μ = 3.56 mm^{-1}, $F(000)$ = 2336, $2\theta_{max}$ = 54°, 15163 reflections collected, 6225 unique reflections, R_{int} = 0.020, 4471 reflections with $I > 2\sigma(I)$, $R[F^2 > 2\sigma(F^2)]$ = 0.040, $wR(F^2)$ = 0.110, S = 1.17.

Conclusion to Ga- and Al-substituted Anderson Molybdates

Two different Anderson molybdate structures were isolated with substitution of the central molybdenum atom by either gallium or aluminum. In both cases, these structures had been described previously, but in the case of the gallium-substituted compound, no crystal structure had been isolated to date. Upon substitution of the central molybdenum atom, the six μ_3-oxo ligands are protonated, which changes the overall charge of the structure from -6 to -3. The synthetic preparation used to isolate these

compounds represents a much-simplified route as well compared to previous isolations.[43,44]

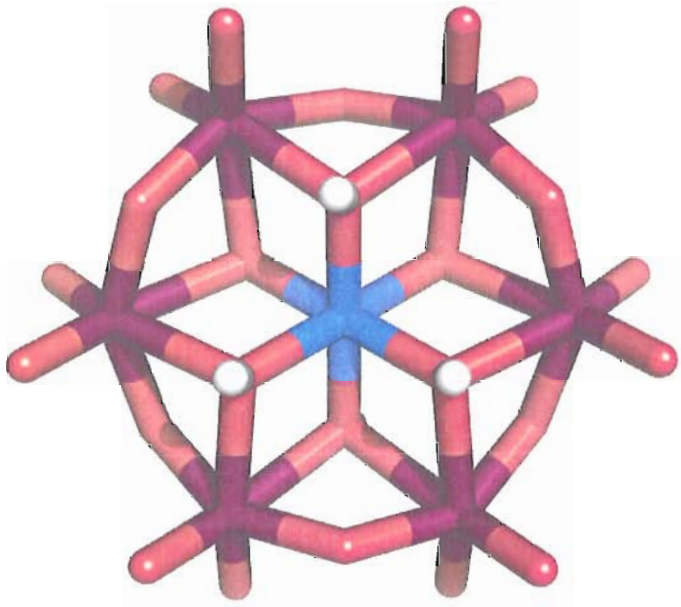


Figure 6.6. PyMOL representation of the crystal structure of $GaMo_6$. This figure depicts the protonated nature of the μ_3-bridges in the structure. Depth can also be well-visualized here. The remaining bridges and capping ligands are all oxo. Gallium is blue, molybdenum is purple, oxygen is red, and hydrogen is white.

Bridge to Chapter VII

This chapter concludes the research results portion of this dissertation. Chapter VII presents concluding thoughts and a summary of the Chapters I-VI. It also contains a number of ideas for future work on this project.

CHAPTER VII

CONCLUSIONS AND FUTURE DIRECTIONS

Introduction

As a graduate education draws to a close, it is only natural to look back on the accomplishments one has been able to achieve. Throughout the ups and (much more numerous) downs, it is necessary to focus both on your successes, to draw inspiration from them, but also on what can be learned from your failures. Because synthetic chemistry is a field of experimentation, success can be in frustratingly short supply. However, at the end of the day, it is both the successes and failures that contribute to your education, and learning from both is absolutely necessary. In fact, it is sometimes even more important to look at what dreams and goals have not been realized. Any good research question leads to further experiments. Not simply to keep ourselves employed, although that is certainly a benefit, but because good science should always lead us to additional questions. Each successful experiment should result in many more questions than answers. For we can never hope to come close to understanding all the intricacies of the natural world, we can simply keep asking ourselves, "Why?". In this spirit, this chapter concludes this dissertation by summarizing the accomplishments described in the first six chapters and proposing future areas of investigation for this project.

Research Summary

The results described throughout this dissertation have had two things in common: 1) the molecules contain Group13 metals and 2) those metals are bridged by hydroxide ligands. The initial review chapter describes the examples of this structural combination in the literature. The molecules covered included both the purely inorganic and those with organic ligands bound to the clusters. Next, Chapter II describes a tridecameric aluminum hydroxide. This compound, $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}]^{15+}$ (**Al_{13}**), was originally isolated by another research group, but only in extremely low yield.[1] Our synthetic procedure afforded the first intentional synthesis of the compound while increasing the amounts that could be isolated.[2] Applying this synthetic procedure to mixtures of $Ga(NO_3)_3$ and $In(NO_3)_3$ hydrates resulted in the isolation of the first ever heterometallic Group 13 hydroxide compounds, as described in Chapter III.[3] The $[Ga_7In_6(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}]^{15+}$ compound described in Chapter III was used successfully as a single-source precursor for solution processed amorphous metal oxide thin films. Building off the initial heterometallic result, Chapter IV describes a whole series of these compounds, encompassing six different Ga/In structures and two different Al/In structures. This represents the largest collection of metal hydroxide compounds reported, as most generally detail only one or two clusters. Chapter V discusses the various attempts to post-synthetically modify these tridecameric clusters. The most successful method so far is a metal exchange procedure where crystals of $[Ga_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}]^{15+}$ (**Ga_{13}**) can be redissolved with MeOH or H_2O with $In(NO_3)_3$ to afford the heterometallic Ga/In compounds. Ligand exchange was also examined, but a

variety of approaches have yet to yield concrete results. Finally, Chapter VI describes four additional Group13 hydroxide structures: two infinite one-dimensional Group13 hydroxy-aceate chains and two Group 13 substituted Anderson clusters.[4,5] The chain compounds consist of gallium or indium metal centers bridged together by two acetate ligands and one hydroxide ligand.[5] The Anderson clusters were originally $Mo_7O_{24}^{6-}$ anions, but the central molybdenum atom has been exchanged for gallium or aluminum atoms and in six μ_3-O ligands protonated to form six μ_3-OH bridges.[4] The results presented in this dissertation represent significant advances in the field, adding a host of new structures, while shedding light on their formation and synthesis.

Future Work

As stated in the introduction, good scientific research should always result in more questions. This research project is certainly no exception. With that in mind, the following sections will describe several areas of research that I think would be particularly interesting to investigate. Some have preliminary results that have been presented already in this dissertation, while others have not yet been discussed.

Oxidation Chemistry

One area of particular interest, one that could potentially be described as the proverbial "low-hanging fruit", would be investigation of the oxidation chemistry that

occurred when Ga_{13} was heated in various solvents, such as toluene, xylene, and hexadecane (Chapter V). In the presence of **Ga_{13}**, about 15 % of the *p*-xylene solvent was oxidized to *p*-tolualdehyde, with an additional 5 % of *p*-toluic acid generated. 55 % of the *p*-xylene remained, in addition to various other byproducts. These percentages were determined by GC/MS analysis. $Ga(NO_3)_3$ also showed some oxidation activity. Determining the differences in reaction products (e.g. product yields, reaction selectivities, and degree of catalysis) could lead to a useful synthetic method for producing these oxidation products from readily available starting materials in a benign method, using molecular oxygen and the gallium compounds.

Metal Exchange

Metal exchange reactions have been examined as a method to access new heterometallic clusters, and this approach has been successful in the case of Anderson and Keggin clusters.[4,6-8] To date this approach has not successfully generated novel structures with the tridecameric cluster framework. However, based on the results with indium substitution in **Ga_{13}**, I believe that if new heterometallic compounds are isolable, the potential is high that this method represents a route to their isolation. While a variety of metals have been examined for metal exchange potential, less has been done in the area of pH control (Chapter V). Only iron was subjected to a variety of pH conditions when attempting to perform metal exchange with $Fe(NO_3)_3$ and **Ga_{13}**. pH variation might be necessary in the case of some metals to facilitate formation of the hydroxide bridges,

as we suspect to be the case in the synthesis of **Al_{13}** (Chapter II).[2] In addition to pH variation, looking at metal salts with other counteranions might be useful. Because we generate the clusters through the nitrate salts of gallium, aluminum, and indium, nitrate salts of potential metal exchange candidates were examined. However, many other counteranions are available, and may be more successful.

Anion Exchange

Anion exchange is another potential way to introduce new metals into the M_{13} framework. There are many known anionic clusters, from the polyoxometallates to copper sulfide clusters.[8] The exchange of NO_3^- anions for these anions would introduce different metal ions into the clusters, and in the case of copper sulfide anions, would potentially generate precursors for materials such as copper-indium-gallium-sulfide thin films which are of interest for solar energy applications.[9,10] To date, anion exchange columns have been used for anion exchange. Running solutions of **Ga_{13}** over Cl^- anion exchange columns resulted in the isolation of powders. These were dissolved with various silver salts, attempting to drive the anion exchange through precipitation of AgCl. Only amorphous powders were isolated from the evaporated solutions. More careful evaporation or vapor diffusion methods might be effective in generating single-crystalline product. Several students have already begun to explore this area more thoroughly, using both anion exchange resins and gel crystallization methods.

Nanocomposite Formation

In the same vein of anion exchange, investigating the interactions of the polycationic M_{13} clusters with negatively charged compounds such as polyoxometallates or Anderson clusters could be a potential area of research. Other research groups have been able to isolate hybrid structures of Keggin-Al_{13} with Anderson clusters, as well as gels formed from vanadium polyoxometallates and Keggin-Al_{13}.[11-14] Initial experiments in this area mixing $\mathbf{Ga_{13}}$ and $Mo_7O_{24}^{6-}$ have led to the isolation of amorphous precipitates which could not be redissolved and recrystallized. Layering experiments to slowly mix the solutions of anion and cation also afforded amorphous materials. However, formation of these powders is highly suggestive of an interaction between the M_{13} clusters and the anionic clusters. The two components are likely coming together too rapidly, not allowing organization into crystalline form. Some of the same methods discussed for anion exchange could be of use here, as the reaction is essentially an anion exchange reaction as well. By further slowing the rate that the solutions mix, it may be possible to form single crystals instead of powders. Gel crystallization might be a way to accomplish this, by trapping one component in the gel while the other diffuses into it.

Ligand Exchange

Of the areas in this future work section, ligand exchange has seen the most prior research, as described in Chapter V. A host of potential ligands and solvents have been tested under various conditions such as heterogeneous, homogeneous, and biphasic. In

all cases tested so far, no single crystalline materials were isolated. However, the ligand-supported structures detailed in Chapter I certainly give credence to the possibility of ligand exchange in these clusters.[15,16] In these syntheses, the ligands have been introduced during the cluster synthesis. It is not known however if the metal hydroxide cluster forms first, and the ligands bind afterward, or if the ligands coordinate first and initiate formation of the cluster element. Experiments utilizing pre-made clusters might help answer this question and shed light on cluster formation—a point of debate.[15,17] As with metal exchange, pH control might be important to achieve ligand exchange. pH control was explored with exchange reactions of the H_3heidi ligand, where pyridine was added as in the literature preparation of Ga_2heidi$_2$, Ga_8heidi$_4$, and Ga_{13}heidi$_6$.[15] Use of a wider range of ligands would also be an area to explore, particularly in the case of biphasic reactions.

Additional EXAFS Studies

Based on the results of full data analysis of previous EXAFS experiments, additional studies could prove useful. Particularly, I think EXAFS might be useful in attempting to answer the question of "regioisomers" addressed in Chapter IV. In the $Ga_{10}In_3$ compounds for instance, we do not know the relative positions of the indium atoms; whether they are all separated from each other by gallium atoms, two are neighboring and one is separated by a gallium atom, or all three are neighboring each

other. If the clusters are stable in solution, EXAFS studies might shed light on this by identifying whether the indium atoms have nearby neighbors that are also indium atoms.

Interactions of M_{13} Clusters with Nucleic Acids

Several research groups have previously examined the interactions of negatively charged polyoxometallate clusters (POMs) with DNA, RNA, and proteins. These clusters have been shown to selectively precipitate prions,[18] hydrolytically cleave RNA model compounds,[19] and inhibit replication of viruses such as HIV.[20] Nanoscience is becoming increasingly interested in using the unique properties of nucleic acid polymers for detection, labeling, and templated synthesis, however molecular scale insight into the interactions between nucleic acids and inorganic clusters is relatively rare. There seems to be a particular lack of knowledge regarding positively charged compounds of this type interacting with DNA, RNA, and proteins.

In order to study and understand the fundamental interactions between positively charged tridecameric Group 13 hydroxide compounds and DNA/RNA, studies to examine the interaction of clusters such as **Ga_{13}** with short DNAs and/or RNAs are proposed. Understanding the interactions between these two types of molecules has implications ranging from mineral catalysis of RNA synthesis to modern pursuits at the bio-nano interface. The similar size regimes present in the two molecule classes (~18 Å for a M_{13} cluster, ~3.5 Å rise/base) should present interesting possibilities to examine different binding interactions. Beyond examining the basic chemical interactions between these two types of molecules, several additional factors could be examined,

including the effects of oligonucleotide length, oligonucleotide sequence, and different metals in the clusters on binding.

Aside from binding interactions, it is known that POMs can cleave the phosphodiester bond of the RNA model compound 2-hydroxypropyl-4-nitrophenyl phosphate (HPNP).[19] Based on previous work showing that $Ga(NO_3)_3$ solutions hydrolyze EtOAc (Chapter VI), $Ga(NO_3)_3$ itself or $\mathbf{Ga_{13}}$ may also hydrolyze the phosphodiester bond in HPNP, which if successful could be expanded to look at actual RNA phosphodiester bonds and whether hydrolysis can be achieved in a specific manner. Because of the relatively small sizes of both nanoparticles and potential nucleic acid chelators a number of characterization methods can be used to understand M_{13}-nucleic acid interactions.

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